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Volume 13, Number 2 Contains

FRONTISPIECE—ACHILLE LE BEL 51

EDITOR'S OUTLOOK 52

METALS AND ALLOYS IN THE CHEMICAL INDUSTRY. I AND II 53
Frederick A. Rohrman

EARLY ZINC WORKS IN THE LEHIGH VALLEY 60
R. D. Billinger

MEASURING THE ABILITY TO INTERPRET EXPERIMENTAL DATA 62
F. P. Frutchey, R. W. Tyler, and B. Clifford Hendricks

APPLICABILITY OF THE LECTURE DEMONSTRATION METHOD TO CERTAIN GROUPS OF STUDENTS 65
Albert L. Elder

A CHAPTER IN TEACHING ACIDS, BASES, AND SALTS 68
P. M. Glasoe

A PLAN FOR THE OPEN HOUSE IN CHEMISTRY 72
Amy Le Vesconte

PROFICIENCY OF FIRST-YEAR STUDENTS IN QUANTITATIVE EXPERIMENTS . 74
Bruce S. Farquhar with Francis Earl Ray

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE ANIONS. CORRECTIONS . . 75

BIBLIOGRAPHY FOR GENERAL CHEMISTRY FROM SEVERAL PERIODICALS. I. 76
Hubert N. Alyea

THE ELIZABETH CLAY HOWALD SCHOLARSHIP 81

SOME TESTS FOR METAL IONS MAKING USE OF ORGANIC DYES 82
Horace M. Tenney and H. J. Long

STILL FOR THE PREPARATION OF BRANDY 83

ELEMENTS OF THE QUANTUM THEORY. VIII 84
Saul Dushman

MATHEMATICAL PROBLEM PAGE 92

LABORATORY PREPARATION OF HYDROFLUORIC ACID 93
Arnold Bookheim

ABSTRACTS 94

RECENT BOOKS 97

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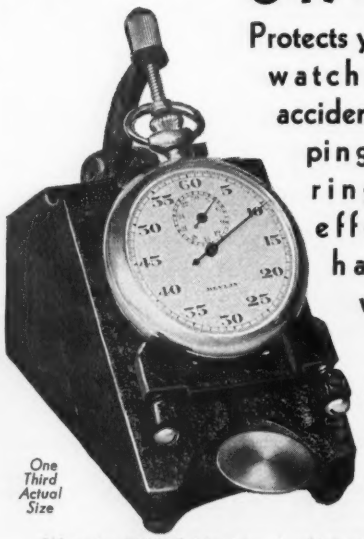

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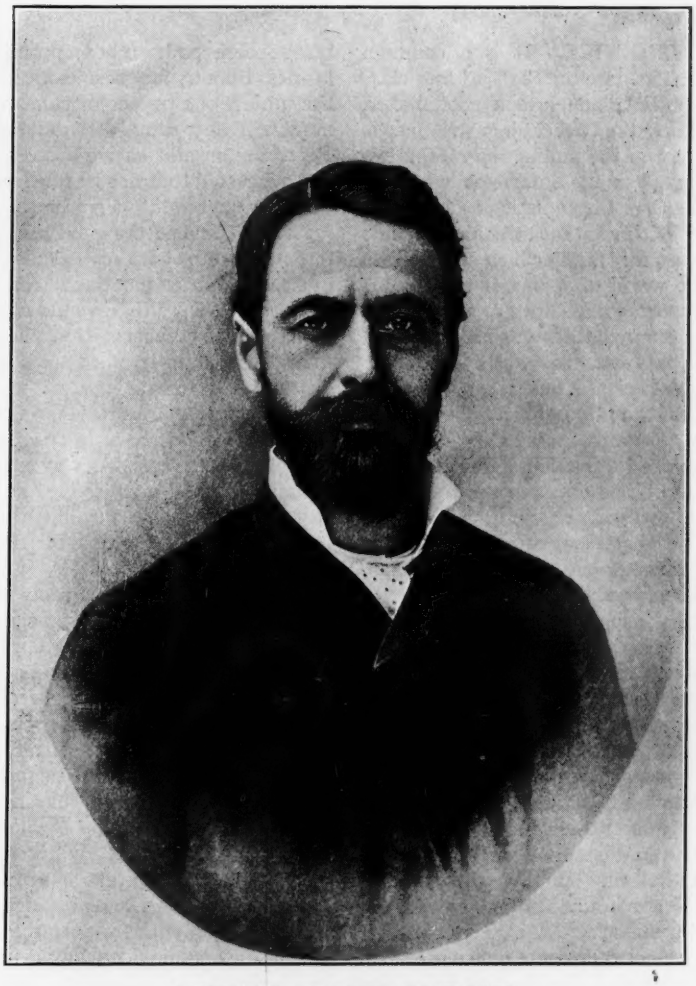

ACHILLE LE BEL (1847–1930)

One of the founders of stereochemistry. He recognized, independently of van't Hoff and at the same time in 1874, that the optical activity of certain compounds of carbon is due to the fact that one of their carbon atoms is attached to four dissimilar groups. At that time he made the prophecy, later verified, that the synthesis of such compounds would yield equal quantities of the optical isomers and that these could be separated by the methods which Pasteur had indicated. In 1891 he prepared the first optically active compound of asymmetric nitrogen, methyl-ethyl-propyl-isobutyl-ammonium chloride. He also carried out engineering researches on Alsatian petroleum and worked on the dimorphism of the chloroplatinates, on the formation of higher alcohols and glycols during fermentation, and on the action of molds and other micro-organisms. (*Contributed by Tenney L. Davis.*)

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EDITOR'S OUTLOOK

MENTAL CALISTHENICS. It is a common belief in sporting circles that a first-class wrestler cannot be made into a good boxer. The explanation offered by the barber-shop wise men is that the overdevelopment of the pulling muscles necessary to good wrestling physique interferes with the speedy operation of the thrusting muscles necessary to good boxing practice. With relation to boxing technic the wrestler is muscle-bound. Similar incompatibilities abound throughout the world of sports, if the convictions of the average sport commentator, amateur or professional, are to be accepted at face value.

These physical data, however trustworthy or otherwise they may be, suggest certain mental analogies. If you listen respectfully to the philosophical discourse of the average competent, but only moderately educated, working man well launched upon his second or third Saturday-night schooner of beer in a respectable neighborhood tavern, he will sooner or later reveal to you tactfully that he suspects the average product of higher education of being a trifle muscle-bound in the head. (Present company, of course, is courteously excepted.) It is easy to dismiss this suspicion as a product of the workings of a defense or compensation mechanism. Nevertheless, your interlocutor can usually point and sustain his thesis with several apt illustrative anecdotes. Moreover, our own experience supplies some incidents that would indicate a certain basis for the working man's suspicion.

Some years ago a younger brother at a fraternity reunion approached us with a guileless air and presented a problem which he said had come up in the course of his work. He was at that time employed in the production department of a manufacturing firm with a view to learning the business from the ground up. A container for the retail packaging of a pharmaceutical product was to be produced. The dimensions of the container—a rectangular can with rounded corners—were specified. The product to be packaged was of such nature and value that its volume would serve as a sufficiently accurate index of its weight, which must be stated on the package. Since the cans were to be paint-decorated in the manufacturing plant, rather than covered with paper labels, it was necessary to know the volume in order that the proper weight might be calculated.

When examined critically, the story exudes a faint odor of herring, but we did not notice that at the time. We immediately reached for a pencil and a blank bridge-score pad. Then, prompted more by mental laziness than by any suspicion that we were being made the subject of a psychological experiment, we paused to inquire if any sample containers had been made up. Receiving an affirmative answer, we stowed our pencil and suggested that one be filled with water and that the water be poured into a graduate.

"That," replied the good brother, "is what my shop foreman did to check my calculations. He told me that my trouble was too damn much education. I just wondered how a Ph.D. would attack the problem."

Lest anyone suspect that the foregoing anecdote is intended to show by none-too-subtle indirection what a clever fellow we are, it may be well to relate a more recent incident. A puzzle-fan friend recently tried the following catch-question on us. A rapidly growing microörganism reproduces by simple binary fission once a minute. A culture dish inoculated with a given quantity of the organism was filled in forty minutes. How many minutes did it take for the dish to become half-filled?

Here we recognized a problem in geometrical progression. We immediately began to plan a procedure of solution about as elaborate as that whereby one calculates the half-life of a radioactive element. It was only after pencil and paper had been denied us and we had been exhorted to use our head that we recognized the obvious fact that the culture must have doubled in bulk in the last minute of the forty-minute period.

We do not, of course, subscribe to the physiological theory that much study is likely to make the brain muscle-bound. Certainly, none of our own lack of quickness on the uptake is attributable to that cause. There is, however, a real danger that too exclusive a preoccupation with formal problems and formal methods of solution may develop mental habits which hinder one from taking convenient shortcuts. It might not be a bad idea to warn students of this danger now and then by practicing a little good-natured trickery upon them in occasional informal quizzes.

The cover picture is a reproduction of Thomas Wÿck's "Alchymist," which hangs in the Karlsruhe Art Gallery. For loan of the photograph from which our cut was prepared we are indebted to Dr. Ralph E. Oesper of the University of Cincinnati.

METALS *and* ALLOYS *in the* CHEMICAL INDUSTRY

FREDERICK A. ROHRMAN

Michigan College of Mining and Technology, Houghton, Michigan

I. INTRODUCTION AND THEORY

INTRODUCTION

THE development in the treatment, production, and transportation of chemicals during the past hundred years has necessitated very great changes in chemical engineering materials of construction. A century ago most of the apparatus and equipment used in the manufacture of chemicals was constructed of wood, iron, copper, and various siliceous materials. Today, because of the much greater volume of chemical manufacture and because of the more complex and corrosive chemicals employed, other constructional materials are called into service. Some must be chosen not only for their corrosion resistance but also for their resistance to high temperatures.

This is truly the age of new metals and complex alloys. No large chemical plant can hope to operate successfully without installations of nickel, silico-irons, nickel-chromium-steels, antimonyl lead, etc. It is quite possible that many of these will give way in the future to more suitable ones.

The purpose of this paper is to outline the developments made in chemical engineering metals and alloys. It is not the writer's intention to omit or disparage the use of glassware, rubber, plastics, and other non-metallic materials, useful as they are; but space permits only what the title of this paper implies. A later article will discuss the use of the non-metallic materials.

REQUIREMENTS FOR METALLIC MATERIALS OF CONSTRUCTION

In choosing the proper metals for an installation or piece of equipment the following factors are generally considered important:

1. Cost
2. Chemical or Thermal Resistance
3. Physical Properties

Cost is probably the most important. Were it not for their high cost, platinum and gold would find considerable use in various chemical operations; their high cost, however, precludes their use except in some isolated cases.

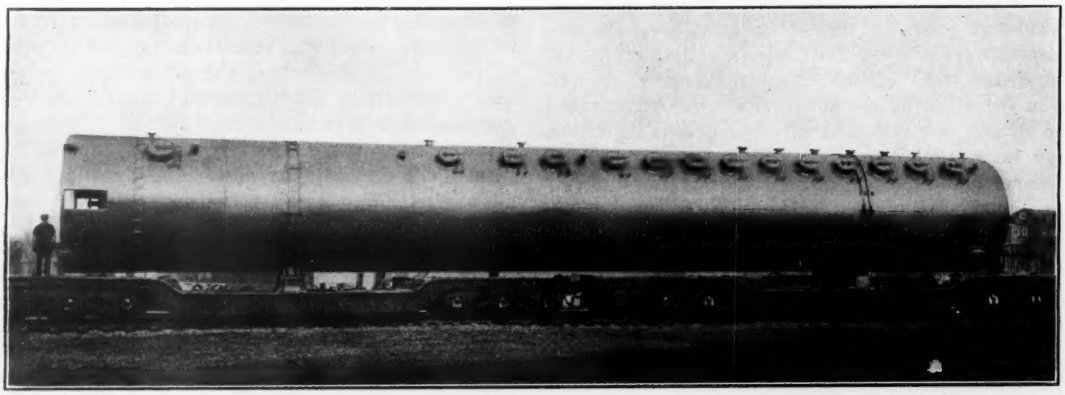
The second most important factor is the chemical or heat resistance of a metal. Obviously, if it is not resistant to the conditions imposed upon it, the material will corrode and ultimately be destroyed. Not only does the corrosion of a metal necessitate the early replacement of that metal but the products of corrosion may so contaminate the processed materials that they become unfit for sale or use. Sometimes a metal corrodes so slowly that it could be used a long time before replacement would be necessary, but its use is impractical because the products of the slight amount of corrosion contaminate the processed chemicals. A good example of this is in the manufacture of phosphoric acid for foodstuffs. From the point of view of equipment life, a certain chromium-nickel-molybdenum-iron alloy is satisfactory as material for the apparatus used in processing this acid. It is slightly attacked, however; and this results in a minute contamination which strict specifications forbid. The very interesting part of this story is that in its place a cheaper iron-silicon alloy is used which does not resist the solutions nearly so well but whose contaminating iron or silicon does not happen to be forbidden by the specifications. If a metal or alloy is not resistant to chemical or thermal action as specified for a certain use then it cannot be used.

Various other factors often have a great deal to do with the choice of material for construction. Very often a balance is struck between an expensive alloy which is resistant and a cheaper one which is not resistant. Many of the more expensive alloys have scrap value which is a good selling point over inferior and cheaper alloys. If the process is in rapid stages of development and improvement, a manufacturer is justified in being reluctant about installing permanent equipment. The same reasoning applies if the market indicates that a lower demand for a certain product is in sight. In such cases more inexpensive and less resistant materials are employed.

In order that a metal or alloy may be fabricated into equipment it must possess properties which permit such fabrication. The desirable physical properties are: machinability, weldability, strength, workability, castability, etc. Some alloys like the silicon-irons and high chromium alloys can be successfully cast, but because they are hard and brittle cannot be machined or worked. Such alloys, which are not amenable to working, can often be cast and ground into intricate shapes and designs. Most of the industrial alloys can be worked and machined with comparative ease, however.

In order to obtain the greatest corrosion resistance some fabricated alloys must be properly heat-treated.

This topic will be discussed more fully later. In recent years the weldability of a material has become more and more important. The advantages of a weld over a riveted or crimped joint should be obvious. Welding, however, often produces a strip along the weld which is more subject to corrosion than the surrounding metal. This difficulty is eradicated by proper heat treatment after the welding operation. Welding has become such a successful art that almost any metal or complex alloy of any size can be joined and finally heat-treated without impairing any of its physical properties or lowering its chemical resistance. Figure 1 shows a huge bubble tower and gas-oil accumulator constructed of $1^1/_4$-inch steel plate. This tower, which is 93 feet high, weighs over 300,000 pounds!



Courtesy Babcock and Wilcox Co.

FIGURE 1.—HUGE BUBBLE TOWER FOR OIL REFINING CONSTRUCTED OF STEEL

Chemical plant equipment is constantly being made larger and larger for the sake of efficiency and economy. The apparatus units are so large in many cases that they must be fitted together outside the fabricating plant. Most of this fitting is done by welding, followed by subsequent heat treatments in enormous annealing furnaces.

In concluding this section one can say that the future points toward cheaper and more resistant alloys bearing better physical properties. The age of alloys has just started; many are the wonders for the future.

CLASSIFICATION

Metallurgists are not satisfied with any one scheme for classifying the various alloys. They speak of ferrous and non-ferrous alloys, however, and that classification seems as good as any for a starting point. For the purpose of this paper it may be justifiable to make a classification for those metals and alloys which have a special significance to the chemist and chemical engineer, as:

Ferrous	*Non-ferrous*
1. steels, wrought, and cast iron	1. aluminum
2. silicon-irons	2. copper, brasses, and bronzes
3. chromium-iron ("stainless steels")	3. lead
4. chromium-nickel-iron ("18-8")	4. nickel and Monel metal
	5. nickel-chromium alloys
	6. rare and miscellaneous metals and alloys

Over ninety-nine per cent. of all installations make use of the metals and alloys given in this classification, although there are a number of metals and alloys not included that find certain isolated uses in the chemical industry. It must be remembered that the use of a certain metal or alloy in a certain process does not necessarily imply that it is the only one that can be used or that it is the best in use. Manufacturers are constantly finding a certain alloy to be more economical or effective than another which they have been using for years.

THEORY

The electrochemical theory of corrosion gives us very definite and useful information concerning the probable behavior of metals in various corrosion media. It tells us, for example, that the metals above hydrogen in the electrochemical series have a tendency to displace hydrogen from solutions according to the Nernst equation. (For a discussion of the mechanics of this theory see the writer's papers in the March, April, and May numbers of the JOURNAL OF CHEMICAL EDUCATION for 1933.) In chemical industry one is concerned with many concentrated acid solutions possessing a very great tendency to dissolve metals with the evolution of hydrogen. If one examines again the class of metals and alloys used in chemical industry he will find that most of them are those which occur above hydrogen and should be easily corroded or dissolved. This truly appears anachronistic, but nature in her display of phenomena has endowed these metals with the protection of self-forming, insoluble, surface-covering films, known to the electrochemist as passive films.

Because of the phenomenon of passivity the large scale chemical industry is possible; without it chemical manufacture would have to be confined to apparatus constructed of glass, ceramics, rubber, rare metals, etc. However, not all metals above hydrogen possess the ability to form passive films, nor are such films formed in all corroding media. Aluminum is insoluble in concentrated nitric acid but not in hydrochloric or sul-

furic; the silico-irons are insoluble in sulfuric acid but not in sulfuric containing chlorides; lead is insoluble in dilute sulfuric acid but not in concentrated; while iron and steel are soluble in dilute but not in concentrated sulfuric acid.

It is unfortunate that so little is known concerning the phenomenon of passivity. Although our experience with the nature of some metals and alloys in various media has given us considerable information as to the probable resistance of other metals or alloys, there is as yet only one infallible rule for determining the adaptability of a metal or alloy, and that is—try it! Certain self-evident rules can be often applied. If, for instance, a high chromium-iron alloy is resistant to crude phosphoric acid and a 20% chromium-iron alloy only slightly resistant, then one can be pretty certain that a 12% chromium-iron will not be very resistant. Again, if nickel is fairly resistant to hydrochloric acid and chromium not resistant, alloys rich in the former will be more useful for solutions of this acid than alloys rich in the latter. Although generally correct, such conclusions may be misleading because of the minutiæ of factors that are involved and not considered.

On the other hand, if a metal or alloy is desired for processing a mixture, for example, of acetic and hydrochloric acid, one would not know what to recommend without actually testing the various metals and alloys in this mixture. One may guess, and guess correctly, at some alloy, but the chances are so great against successful guesses "backed by reason" that it does not pay. Too often metals are tested against a specified solution, recommended for service, only to fail in actual use, as manufacturers are keenly aware. For instance, if a metal is desired for phosphoric acid, tests are carried out at different concentrations of the pure acid and at different temperatures, and on the basis of the results a final recommendation is made. However, the tests are made in pure acid, while the acid used in processing is not pure (in one instance it contained one half per cent. hydrofluoric acid, which makes it a much more corrosive solution than the pure acid); consequently, the chances that the recommended alloy will stand up are very poor.

The eager desire of the metal salesman to sell his products "with hopes" and the laxity of the user in defining the conditions under which the metal will be used have caused much grief for both parties. Some time ago the writer wrote to a number of manufacturers of metals and alloys asking for samples resistant to a certain solution. Over sixty different samples were obtained, thanks to the kindness and interest of these concerns, but only two were found fairly resistant and one resistant! Writing to the several companies processing this solution the author found twenty alloys and metals in use amid much grumbling and discontent.

It may be correct to say that for every process there is one, and only one, metal or alloy which works best. All others, then, must be inferior in a lesser or greater degree. It is up to the metallurgist and chemical engineer to find which is best. To date, this job has not been done thoroughly, although the future indicates that it must and will be efficiently accomplished.

II. FERROUS METALS AND ALLOYS

IRON AND STEEL

Iron and steel, being relatively inexpensive and possessing desirable physical properties, are used more, where conditions permit, than all the other metals and alloys put together. Iron and steel are used not only with the less corrosive substances but often with the strongest acids. This is due to two reasons, first, the low replacement cost for iron and steel equipment and second, the fortunate passive behavior of iron in various media.

Aside from their use for general plant constructional equipment, iron and steel are used for equipment and apparatus designed for water and steam, weak electrolytic solutions, water-free gases and liquids, alkaline and ammonia solutions, solid and liquid caustic, molten aluminum, zinc and brass, petroleum and its products, and concentrated nitric and sulfuric acids, and their mixtures. The use of iron and steel for jacketing and reinforcing more resistant materials is steadily becoming more common. Figure 2 illustrates a large mixing kettle for processing phenolic compounds which is constructed chiefly of cast iron and is reinforced with a sheet-steel jacket.

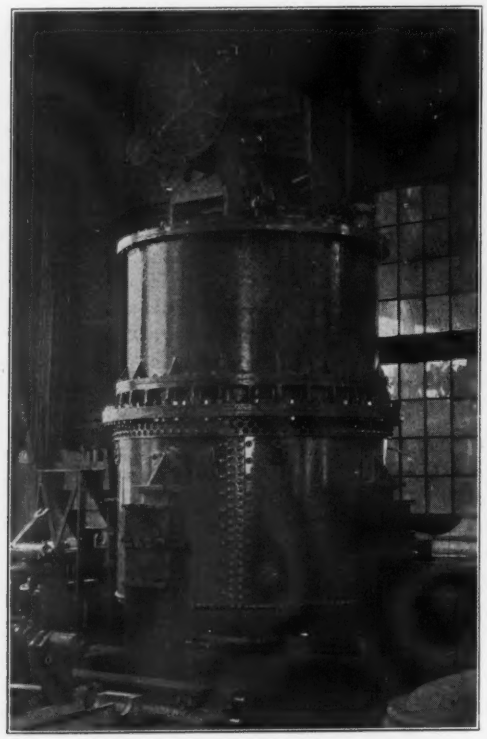
It would be futile to attempt any precise differentiations between iron, wrought iron, and steel. Cast iron may be said to contain several per cent. carbon and various impurities. A typical analysis would be: 2.0–4.5% carbon, 0.7–3.0% silicon, 0.1–0.3% sulfur, 0.1–3% phosphorus, 0.2–1% manganese, and traces of other impurities. It is quite hard and brittle; these characteristics make it suitable only for castings which will not be subject to shock or impact. Wrought iron is made from cast iron by oxidizing most of the impurities out of the former in a basic furnace. It is soft, tough, and malleable and possesses a fibrous structure because of slag inclusions. Steel is generally considered as a form of iron containing less than 2% carbon and being susceptible to hardening through heat treatment.

Because of the ease of casting and because of its cheapness, cast iron is used where conditions permit. It finds uses in the manufacture of caustic pots, although the use of nickel or nickel-cast iron is considered to be better. Figure 3 illustrates a large reaction kettle constructed of cast iron for the manufacture of a dyestuff. Cast iron is also used to a great extent for molten aluminum and its alloys, zinc, brass, solders, copper, and several other metals and alloys.

Wrought iron, though being gradually replaced by mild steel, possesses excellent resistance to water. This property is probably enhanced by its high silica con-

tent. On the other hand, the high silica content is responsible for the lack of resistance of wrought iron to molten alkali and strong caustic solutions.

The excellent physical properties of steel and its ease of fabrication make it a very desirable metal for construction where corrosion is not severe. The phenomenon of passivity permits most steels to withstand strong sulfuric and nitric acids as well as their mixtures (mixed acid). Nitric acid can be handled if it is over 65% HNO_3; below this concentration the iron ceases to retain the passive state and passes into solution very readily. Sulfuric acid can be handled in iron equipment when it is from 78–98% H_2SO_4. Sulfuric acid or mixed acid ($HNO_3 + H_2SO_4$) containing more than 20% water attacks most steels because at these lower concentrations they are not rendered passive. Iron and steel containing much silicon are selectively corroded



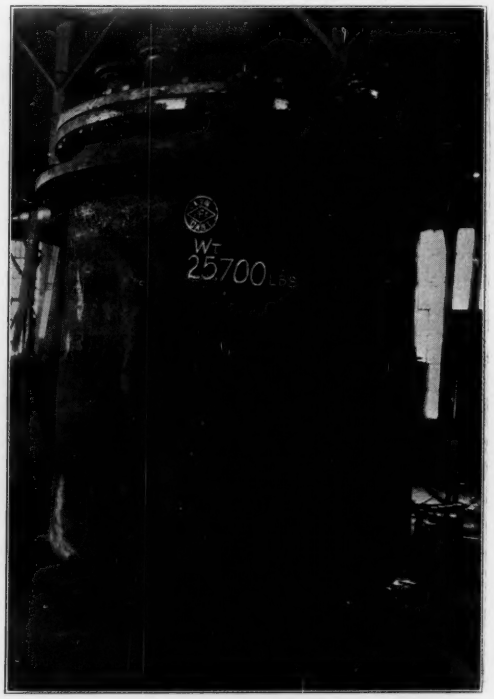
Courtesy Buffalo Foundry and Machine Co.

FIGURE 2.—REACTION VESSEL CONSTRUCTED OF STEEL AND CAST IRON

at the grain boundaries by sulfuric acid containing over 100% H_2SO_4 (oleum). This is due to the action of SO_3 on silicon, the latter being oxidized to SiO_2. It is therefore important that iron used with fuming sulfuric acid contain very little silicon.

The absence of electrolytic action in the absence of water makes it possible to employ iron or steel with dry chlorine, HCl, SO_3, bromine, etc. In the alkali-chlorine industry the wet chlorine is dried by sulfuric acid, and from this point the gas is transferred, compressed, and liquefied in steel equipment without danger of corrosion. Liquid HCl gas is also transported in steel cylinders.

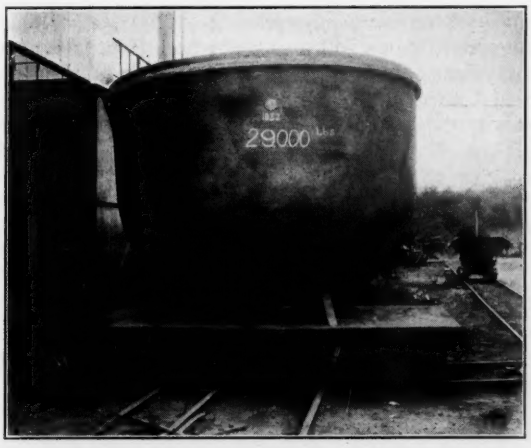
The use of iron for electrodes in many electrolytic processes is very common, its chief use being as cathodes in the alkali-chlorine industry whereby salt solutions are electrolyzed. In the electrolysis of sodium hydroxide solutions for the production of oxygen and hydrogen, iron is sometimes used for the cathode. The Edison storage cell also makes use of iron cathodes.



Courtesy Lynchburg Foundry Co.

FIGURE 3.—REACTION VESSEL FOR DYE MANUFACTURE

In recent years there has been a great tendency to investigate and use steels containing low percentages of nickel, molybdenum, copper, chromium, silicon, and vanadium. Figure 4 shows a large caustic pot for boiling down caustic solution. Such pots are often made of iron alloyed with small amounts of nickel. The indications are that such additions improved the chemical resistance for certain purposes as well as the physical properties in general. The petroleum industry has some very severe corrosion- and heat-resistance problems which still remain unsolved. In the cracking of oils to produce lighter fractions, the use of the proper metal for the cracking tubes is a difficult problem. The unfortunate tendency for the tubes to burst is well known. The advantage of the straight steel or low alloy steel tubes, such as 5% chromium, lies in the fact that any tendency which they may have for failure announces itself by a swelling and the operator can then "cut them out." The disadvantage of the higher



Courtesy Lynchburg Foundry Co.

FIGURE 4.—CAUSTIC POT MADE OF SPECIAL ALLOY CAST IRON

alloys of iron is due to their failure without any preliminary warning.

The use of iron and steel at higher temperatures is limited because of the rapid rate at which oxygen and iron react as the temperature is increased. The action is direct, with the formation of a non-adherent oxide scale. The rate of reaction increases very rapidly above 200°C. For temperatures above this point special alloys are called into use. These will be mentioned later.

THE SILICO-IRONS

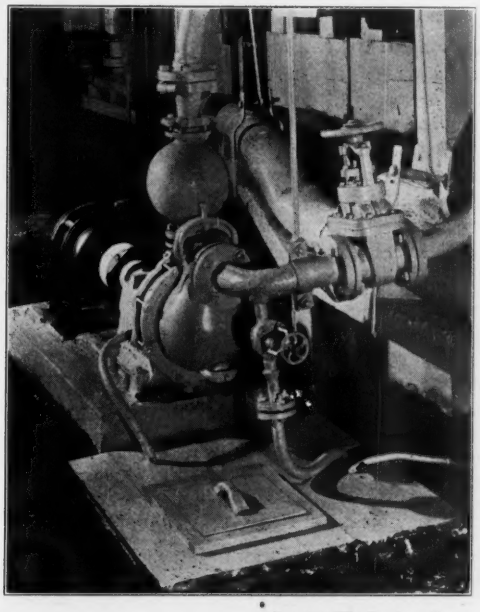
The addition of silicon to iron produces no beneficial effects until about 13% has been introduced. Alloys of about 14% to 17% silicon seem to be the ideal compositions for corrosion resistance. The addition of over 17% silicon produces a slight lowering in chemical resistance.

The earliest manufacture of the silico-iron alloys was attended by a great number of difficulties, chiefly physical in nature. It is now known that the iron and the alloying agent must be low in impurities, such as sulfur and phosphorus, in order to produce successful castings. The casting temperatures as well as the cooling rates are also very important. The alloys are very hard and brittle and are difficult to machine or work. All fabricated equipment or apparatus must be cast into the desired form and then ground with abrasives to the proper fitting. Figure 5 illustrates a Duriron pump set up for ammonium sulfate solutions.

Duriron and Corrosiron are the trade names for the most important silico-iron alloys used in this country. The manufacturers of these alloys have been very successful in fabricating them into apparatus of desired shapes and sizes. Without doubt, these alloys are so widely used with so many corrosives that it would be simpler to list the general groups of corrosives they will not resist than those they will resist. The use of both Duriron and Corrosiron would undoubtedly be greater if they possessed better physical properties.

The avidity with which the halogens and halogen acids attack most metals and alloys is well known. The straight silico-irons are no exceptions in this respect. As previously mentioned, the action of strong alkali and molten caustic upon silicon is rather pronounced. It is evident then that these alloys are not to be used with such substances. Further, the heat conductivity of these alloys is not as good as that of cast iron. Consequently, apparatus constructed from large castings is very sensitive to rapid temperature changes. These silico-iron alloys are, also, not recommended for very high pressures except for smaller apparatus.

Very recently a new silico-iron alloy appeared bearing a composition of 13.5 silicon, 3.5 molybdenum, and 1.0 nickel. This new alloy, called Durichlor, possesses exceptional resistance to hydrochloric acid and is probably the only alloy existing which resists this corrosive



Courtesy The Duriron Co.

FIGURE 5.—DURIRON PUMP FOR PUMPING AMMONIUM SULFATE LIQUORS

at all concentrations and temperatures. This resistance is attributed to a protective compound film which forms on the surface after a definite period of exposure. An interesting bit of information relative to this alloy is that it was not developed specifically for the purpose of resisting hydrochloric acid but was made in an attempt to improve the properties of Duriron, its HCl-resisting properties being discovered later.

THE CHROMIUM AND CHROMIUM-NICKEL IRONS AND STEELS

These series of alloys are of relatively recent origin, dating from about the start of the World War. Today (known to the man on the street as "stainless steels") they are probably more common than any other series

of alloys. Actually, they are far from being stainless; a more appropriate designation would be "corrosion and heat resisting" steels.

The alloys having the greatest importance in these series may be classified as follows:

Cr-Fe	Cr-Ni-Fe
Low Cr (11–15%)	High Cr—Low Ni (less than 3%)
Medium Cr (17–20%)	"18-8" (18 Cr-8Ni)
High Cr (24–30%)	High "18-8" (20–27 Cr-12–24 Ni)
	High Cr-Ni (27 + Cr − 14 + Ni)

Many other alloys of chromium, nickel, and iron do exist, but those above seem to be of the greatest importance.

The properties and consequent uses of these alloys may be explained without taking too many liberties with the governing fundamentals by saying that all these alloys are resistant because of their tendency to form insoluble oxide coatings. The addition of both nickel and chromium improves the chemical resistance, the chromium additions having no effect until 11% chromium is reached. As the nickel and chromium contents are increased the chemical resistance against most corrosives improves correspondingly.

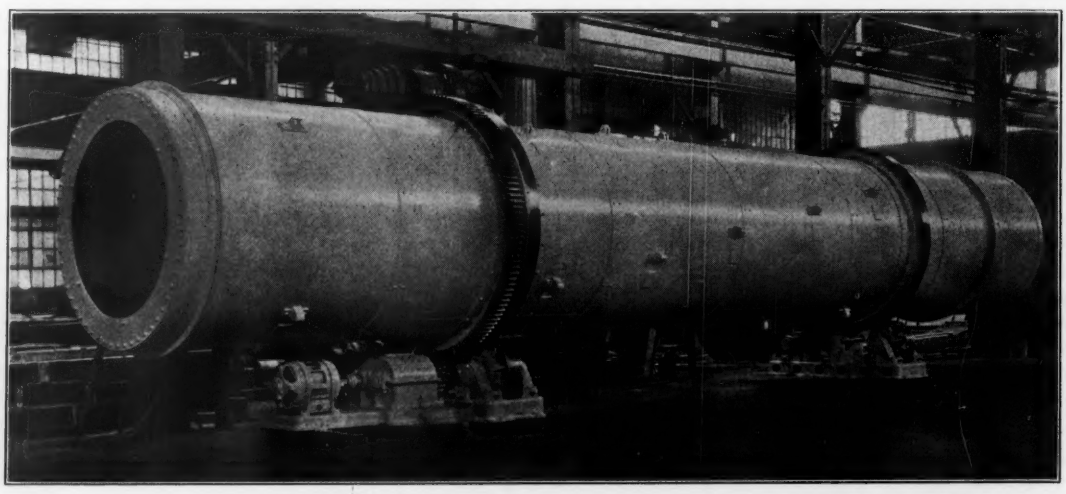
With the straight chromium-iron alloys an increase in chromium (over 11%) improves the chemical resistance while the physical properties become poorer. On the other hand, the opposite effects are noted for the carbon contents of such alloys. It is therefore important to get a balance between the chromium and carbon percentages in order to have an alloy which will have good chemical resistance as well as desirable physical properties. In this way a 12% chromium alloy may have a 0.10% carbon content; an 18% alloy may have a 0.25% carbon content; and a 27% alloy may have a carbon content as high as 0.75%. In cases where hardness and strength are not as important as chemical resistance the carbon content is lowered. The chromium-iron series crystallizes in the body-centered cubic system, commonly called the ferritic state; this is characteristic of a soft annealed iron. Heat treatment rarely improves its physical properties, because of the great tendency for chromium to crystallize only in the body-centered cubic system.

These alloys show excellent resistance to nitric acid, being probably unexcelled for this purpose, They are also used in contact with various kinds of fruit juices, as well as with many of the weaker acids, such as acetic. The mineral acids such as hydrochloric, crude phosphoric, and sulfuric corrode these alloys readily, although phosphoric has little effect upon the higher chromium alloys. Figure 6 shows a large rotary drier constructed of "stainless steel" which is employed for drying a corrosive metallurgical product.

The addition of one to three per cent. nickel to the chromium-irons and steels tends to improve the physical properties greatly. A very large number of such alloys are used where high temperatures are employed. They can be used at temperatures around 1500°F. without danger of disintegration or warping. Figure 7 illustrates a large SO_2 blower whose impeller is constructed of nickel-chrome steel.

The most important alloys of the entire chromium-iron and nickel-chromium-iron series are the "18-8" alloys containing 18% chromium and 8% nickel. In contrast with the straight chromium-iron alloys these alloys are austenitic by virtue of the tendency to crystallize in the face-centered cubic system under the proper heat treatment. The presence of carbon then is not necessary or desired; in fact, the tendency is to try to remove every trace of graphitic carbon because of the dangers of intercrystalline corrosion.

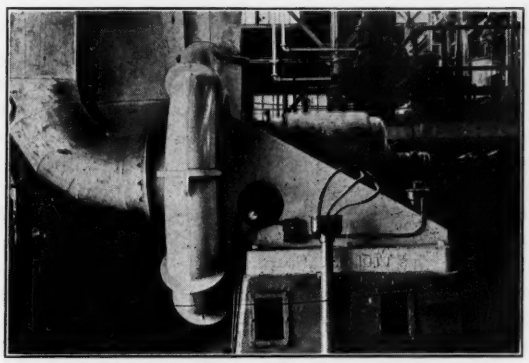
The tendency for these alloys to precipitate carbides at the grain boundaries upon cooling and give local points for local-action corrosion has been a problem worrying the manufacturer and alloy user for years. This type of corrosion, commonly called intercrystal-



Courtesy Struthers-Wells Co.

FIGURE 6.—"18-8"-LINED DRIER FOR CORROSIVE ORES

line corrosion, intergranular corrosion, or embrittlement, is characterized by a tendency for corrosion to confine itself chiefly to the grain boundaries and thus to cause eventual disintegration of the alloy.



Courtesy Elliott Co.

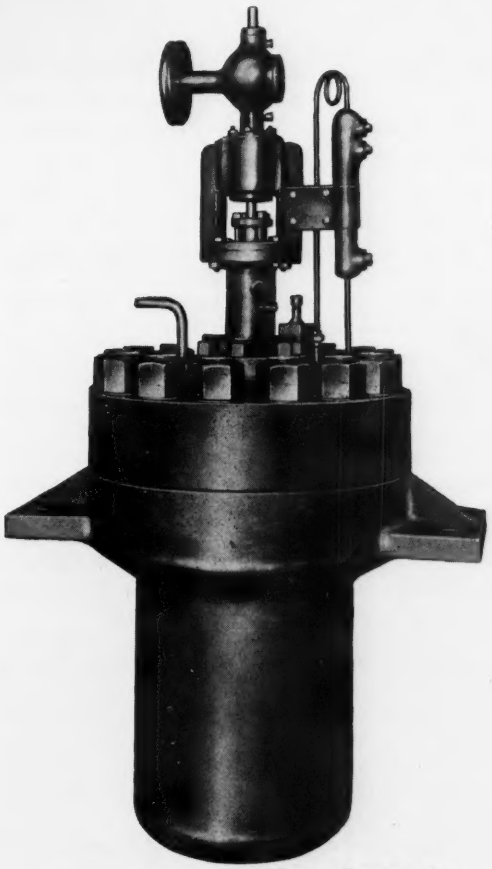
FIGURE 7.—BLOWER FOR SO_2 CONSTRUCTED OF STEEL AND NICKEL-CHROMIUM-STEEL

Intercrystalline corrosion is combated in these alloys in three ways: by limiting the carbon content to 0.07 per cent., by proper heat treatment, or by the addition of small amounts of metals such as molybdenum, silicon, titanium, or columbium which tend to hold the carbide phase in solid solution. Such alloys are called "S" alloys (the "S" signifying soft); thus a straight "18-8" alloy might be called KA_2 or "18-8" steel, while the stabilized alloy might be called KA_2S or "18-8 S." It is only fair to mention that intercrystalline corrosion is not an inherent property of these alloys only, but exists in hundreds of other metals and alloys as well. Merely because the "18-8" alloys have enjoyed such wide use has the intercrystalline corrosion study centered upon them.

Many alloys exist having the composition 24 Cr, 12 Ni, or 24 Cr, 12 Ni, 3 Mo. Such alloys are fabricated for the sole purpose of obtaining more corrosion resistance than the "18-8" or "18-8-3" alloys can offer. The alloys of higher chromium-nickel composition, such as 36 Cr–20 Ni, or 35 Ni–15 Cr, find their chief use as heat-resisting alloys.

The "18-8" alloys find most extensive uses in the chemical industry. Recently, the "18-8-3" alloys have been found very useful in the manufacture of crude phosphoric acid and in the sulfite treatment of paper pulp. The milk-handling and pasteurizing industry uses "18-8" alloys to a great extent. The breweries are also employing the alloys. While these alloys are not quite as resistant to nitric acid as the chromium-iron alloys, they are better for sulfuric acid and find a much wider use in the food-processing industries because of their better physical properties. Again, it is probably easier to state which reagents attack these alloys rather than which do not. The halogens and their acids are the worst offenders, along with most boiling acids. The molten metals also attack these alloys.

Reactions involving hydrogen or hydrocarbon at high temperatures and pressures place unusual demands upon metallic equipment. The difficulties in such reactions are due to hydrogen penetration and combination with the alloyed or precipitated carbon which result in eventual intercrystalline corrosion of a different kind. Manufacturers have avoided most of these difficulties by lowering the carbon and raising the metallic alloy contents of these alloys. Figure 8 illustrates a stainless steel autoclave for hydrogen which operates at over 3000 lb. per square inch pressure.



Courtesy Blaw-Knox Corp.

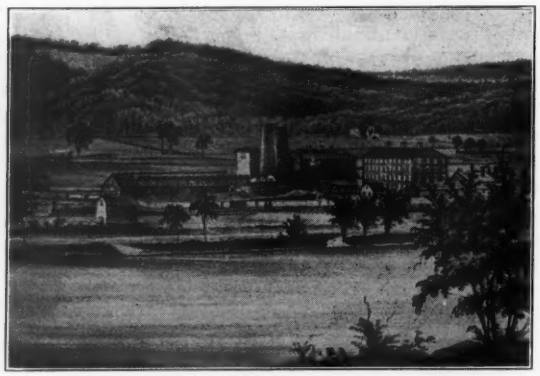
FIGURE 8.—25-GALLON HYDROGEN AUTOCLAVE WITH "STAINLESS-STEEL" LINING

These alloys can be welded, but inasmuch as the welding operation produces a temperature gradient ranging from the molten weld to the cold body of metal, carbide will be encouraged to precipitate if the alloy contains none of the stabilizing elements mentioned. The alloy must then be annealed above 1800°F. and be properly heat-treated so as to redissolve the precipitated carbide in order to retain its corrosion resistance.

EARLY ZINC WORKS *in the* LEHIGH VALLEY*

R. D. BILLINGER

Lehigh University, Bethlehem, Pennsylvania



M. S. Henry's "History of the Lehigh Valley" (1860)
PENNSYLVANIA & LEHIGH ZINC COMPANY'S WORKS

THE PRODUCTION of zinc on an industrial scale, according to Ingalls, (*1*) was first undertaken in England by John Champion, who erected works at Bristol, England, in 1740. In the United States successful zinc smelting was not accomplished prior to 1850.

This paper is concerned with the zinc works located in Bethlehem, Pennsylvania, in 1853. At first constructed for the production of zinc oxide, the plant soon undertook separation of metallic zinc. The plant continued to produce these products at the above location until its absorption by the New Jersey Zinc Company and the removal of the plant in 1911.

The location of a zinc works in Bethlehem followed the discovery of zinc ores in the Saucon Valley near Friedensville, about three miles south of Bethlehem. Peculiar minerals were noted in this neighborhood early in the nineteenth century. Farmers were alert for iron ores which were worked not far distant. About 1830 (*2*) some curious person hauled a wagon-load of the unknown ore to the Mary Ann iron smelter in Berks County. An unsuccessful attempt was made to determine its nature, the failure being due to the volatilization of zinc at the high temperature of the iron furnace.

The character of the ore was not definitely known until Mr. W. T. Roepper examined it and discovered it to be calamine, the hydrosilicate of zinc. Roepper was a local mineralogist who later became the first professor of mineralogy at Lehigh University. He conducted experiments in Lehman's foundry in South Bethlehem and, while not successful in isolating zinc from the ore, he did make brass by smelting calamine and native copper.

Outside interests were next consulted with a view to furthering the project. A Philadelphia importer, Robert Earp, was induced to lease the Ueberroth farm, on which the ore had been discovered. Nine tons of ore were mined and shipped to England to be tested. Again an unsuccessful report was returned, perhaps because the English process used a higher temperature in roasting ores.

At this point Samuel Wetherill, a Philadelphian with previous experience in the production of zinc oxide, became interested in the newly discovered ore. Wetherill (*3*) came from a family of inventors and was scientifically minded. His great-grandfather, Samuel Wetherill, had produced the first white lead made in America. His father, John Price Wetherill, had been vice-president of the Academy of Natural Sciences. Young Wetherill had worked in the plant of the Belleville White Lead Company of Philadelphia, where he learned the art of making lead pigments. In 1850 he attacked the problem of utilizing zinc ores and endeavored to determine whether zinc oxide could be substituted for white lead as a paint pigment.

Wetherill's experiments with zinc oxide led to his engagement with the New Jersey Zinc Company. In 1852 he perfected a method of preparing zinc oxide directly from zinc ores. In France, Le Clair had been knighted for discovering a method of making zinc oxide. The French method involved the reduction of the ore to spelter, with subsequent burning and subliming of the oxide in fire-clay tubes. Wetherill's "furnace process" was distinct and new. It consisted in reducing mixed coal and ore by the direct action of heat and a cold blast upon a furnace bed having small holes, each producing the reducing flame. The zinc vapor formed was instantly oxidized, and the zinc oxide was blown with the gases into settling chambers where ashes and coarse particles were deposited. Finally, the pure zinc oxide was strained from the gases by large flannel and muslin bags. The last part of the operation was the invention of Mr. Richard Jones.

It was this process which was used in the first Bethlehem plant. With the aid of some New York capitalists the Zinc Metal Works of Gilbert, Wetherill, Baxter, and Company was organized. A location on the south side of the Lehigh River, opposite Bethlehem, was selected. Four acres of land were purchased from Augustus Luckenbach, the site consisting of a triangle of land enclosed by the Lehigh Valley and North Pennsylvania Railroads. That section was then called Augusta, later Wetherill, but is now part of Bethlehem

* Presented before the Division of History of Chemistry at the eighty-ninth meeting of the American Chemical Society, New York, April 22, 1935.

in the area known as the south side. Besides the favorable location with respect to railroads, the plant had also the advantage of proximity to the Lehigh Canal on which coal was being hauled from the anthracite regions.

A plant was erected at a cost of $85,000. The construction began in April, 1853, and the work was nearing completion when, on July 9th, a tornado swept the valley and demolished the main building. Work was quickly resumed and by October 13th of the same year the furnaces began to produce zinc oxide.

The first output of the new plant was produced at the rate of four tons of zinc oxide per day. The product was worth six and one-half cents a pound. The production of zinc oxide in Bethlehem from the Friedensville ore was the second successful venture of its kind in the United States. Hitherto, less than 3000 tons had been produced at Newark by the New Jersey Zinc Company, which had started production in 1852.

Now a thriving industry had sprung up in Bethlehem, producing about $300,000 worth of merchandise annually. In the six years from 1854 to 1860 some 40,000 tons of zinc ore were mined at Friedensville, and hauled over South Mountain by mule team to be treated in the furnaces along the Lehigh River.

A good account of the early years of this zinc works is recorded by M. S. Henry (*4*) in his "History of the Lehigh Valley," published in 1860. The picture of the plant shown here was copied from the lithograph illustration in Henry's history.

The Company was reorganized and renamed in 1855 when the Pennsylvania and Lehigh Zinc Company was incorporated on May 2nd, "for the purpose of mining zinc ore, and other ores found in connection therewith, and of manufacturing zinc paint, metallic zinc, and other articles, from said ores in the counties of Lehigh and Northampton, and of vending the same." The capitalization was $1,000,000, and the directors and most of the stockholders of the company were Philadelphians.

Mr. Wetherill continued as superintendent of the works until September, 1857, when he was succeeded by Joseph Wharton. During Wetherill's administration 4725 tons of zinc white were produced. He had tried many experiments to produce spelter, but, although a few tons were made, the process was not economically practicable.

In 1859 Wharton contracted with a Belgian firm for the erection of smelting works of the Belgian type. The reduction of zinc ores in small retorts had been successfully accomplished in Belgium as early as 1805 by the Abbé Daniel Dony, a chemist of Liége. A number of Belgian workmen, under the leadership of Louis De Gée, supervised the construction of the new plant. The Belgian furnaces began operations in July, 1859. These were the first entirely successful zinc furnaces in the United States. Previous operations in the production of spelter had been made about 1850 in New Jersey, but the presence of iron oxide in the franklinite ore had limited the initial success of this attempt.

The Belgian process, similar to present-day methods, employed cylindrical retorts placed in rows, gently inclined, in the furnace. The preparation of charges for distillation consisted in mixing the calcined ore with a proper proportion of coal. The flames from the coal burned in the furnace played around the clay retorts. When zinc vapors appeared at the ends of the condensers, conical caps of sheet iron were attached. Every twelve hours the zinc was collected in ladles and poured into molds.

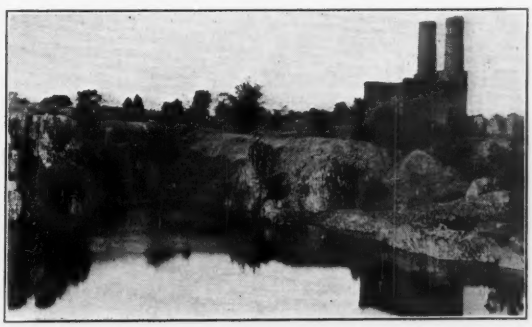
In 1860 the name of the company was changed to the Lehigh Zinc Company. In April, 1865, the rolling of sheet zinc was added to the operations of the company. By 1877 the list of names on the company's payroll numbered seven hundred. In 1881 these works were taken over by the Lehigh Zinc and Iron Company, which added to its previous operations the production of spiegeleisen.

An excellent account of the mining and metallurgical methods practiced by the Lehigh Zinc Company is given by H. S. Drinker (*5*), a young mining engineer, who later became President of Lehigh University.

The quality of the zinc produced in Bethlehem was very high, as shown by the following note (*6*) in the *American Chemist* of May, 1871:

Composition of Commercial Zinc (spelter). The following analyses of spelter were executed by the senior editor some five years since, and may prove of interest to our readers as showing the great purity of the American product, the Lehigh and the New Jersey in comparison with the imported, the Silesian and Bleiberg:

	Silesian	*Bleiberg*	*Lehigh*	*New Jersey*	*La Salle*
Zinc	97.471	98.054	99.982	99.976	99.378
Lead	2.393	1.536	..	..	0.530
Cadmium	trace	0.282	..	..	0.078
Iron	0.136	0.101	0.018	0.024	0.041



RECENT VIEW OF FRIEDENSVILLE MINE, NOW A FAVORITE SWIMMING HOLE

In 1875 the Lehigh Zinc Company produced 1505 tons of metallic zinc, the third largest production of some thirteen companies then in operation.

The zinc ores used came from the Friedensville region where Roepper first recognized calamine. As mining progressed the calamine decreased and zinc blende, pyrite, and marcasite predominated. This district also furnishes ore for the Passaic Zinc Company, and the Bergen Point Zinc Company in New Jersey. In 1881

the Friedensville Zinc Company was organized and smelters were erected close to the mines. Mining operations continued in this region until 1893, when activities were suspended due to excessive cost of pumping water from the mines.

It has been estimated that 50,000 tons of spelter and 90,000 tons of zinc oxide, valued at about $20,000,000, were produced from The Friedensville Zinc ores.

The Lehigh Zinc Company contracted for a time with the New Jersey Zinc Company for zinc ores from the New Jersey mines. In 1897 a consolidation of the Passaic Zinc Company, the Lehigh Zinc Company, and some western zinc works was accomplished by the New Jersey Zinc Company. Soon after the consolidation the site of Palmerton, 24 miles above Bethlehem, on the Lehigh River, was chosen for the location of what is now the largest zinc plant in the country.

In 1911 the works at Bethlehem went permanently out of use. The old location is now occupied by shops of the Bethlehem Steel Company. A zinc oxide plant is still maintained at Freemansburg, several miles down the Lehigh River. Although the Friedensville mines have not operated since 1893, there is plenty of good ore in the region and, despite the pumping problem, mining operations may again start when economic conditions warrant.

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MEASURING *the* ABILITY *to* INTERPRET EXPERIMENTAL DATA*

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B. CLIFFORD HENDRICKS

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THE American Council of Education through its Coöperative Test Service is helping college teachers to become more critical of their examinations. In science, expression of that need for more adequate tests is voiced in such statements as: "Skilled help is needed by the teacher in building tests for such intangible objectives as ability to infer, ability to use the scientific method of thought, and ability to apply the principles of chemistry."[1] College teachers are also reëxamining their aims in an effort to be sure for just what they should test.[2] Some provisional test forms have been suggested for the application of principles.[3,4] This paper is reporting an attempt to provide a measure for another of the less tangible but desired outcomes of chemistry instruction.

Teachers of chemistry are interested in helping their students interpret data obtained from experiments new to the students. This constitutes one of a variety of objectives of the teaching of chemistry. This objective, when expressed in terms of the behavior of students, often means that when students are presented with experimental data new to them, they will formulate and state interpretations which may reasonably be made from the data. Various kinds of experimental data, such as tabulations, graphs, and qualitative statements, may be presented to the students and in such an examination they may be expected to react to each set of data in turn. Since the objective is to teach students to interpret data which are *new* to them, data with which students are unfamiliar must be presented. One source of these data consists of recent chemical literature containing the reports of chemical experiments. This precaution precludes the possibility of parrot-like repetition of memorized interpretations and makes it necessary for the students to formulate their own inter-

* Presented at the eighty-ninth meeting of the American Chemical Society before the Division of Chemical Education, New York, April 26, 1935.

[1] O. M. SMITH AND B. CLIFFORD HENDRICKS, "Service tests for chemistry," *Sch. Sci. Math.*, **35**, 488–91 (1935).

[2] O. M. SMITH, "Accepted objectives in the teaching of general college chemistry," J. CHEM. EDUC., **12**, 180–3 (1935).

[3] FRED P. FRUTCHEY, "Measuring ability to apply principles of chemistry," *Educ. Research Bull.*, **12**, 255–60 (1933).

[4] B. CLIFFORD HENDRICKS, RALPH W. TYLER, AND FRED P. FRUTCHEY, "Ability to apply chemical principles," J. CHEM. EDUC., **11**, 611–3 (1934).

pretations. Some students can repeat from memory interpretations which were made for them but cannot interpret new data for themselves. Other students, who do not know and cannot repeat interpretations which others have made, can make reasonable interpretations if given the experimental data.

The achievements of students are quite different in different objectives of teaching. To obtain a clear, comprehensive picture of the students' achievement in chemistry it becomes necessary to collect evidence of achievement in each of the important objectives of chemistry teaching.

The behavior expected of students in interpreting experimental data is their own formulation and statement of interpretations. Two examples of the kind of exercise used to collect this evidence are given below.

TYPE I TEST FORM

Directions: In each of the exercises on the following pages an experiment is described. Read the description of each experiment. Assume that the facts given in the description of the experiment and in the results obtained are correct, then on the basis of *these facts only* write the conclusions you could reasonably draw from the results obtained in this experiment.

A. In an experiment some white starch was treated with brown iodine solution. This was done ten times and each time a blue color was formed.
Later some white starch was mixed with saliva. The mixture was left for a time and then treated with brown iodine solution. This was done ten times and each time no blue color was formed.

Write in the space below the conclusions you could reasonably draw from the results obtained in this experiment.

B. Sixty plates of the same size were cut from a piece of blue annealed tank steel. Twenty plates were coated with zinc to a thickness of 0.007 inch; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
Twenty plates were coated with cadmium to a thickness of 0.007 inch; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
Twenty plates were not coated; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
The corrosion deposited on each of the 60 plates over a period of 7 days was carefully weighed and the results were tabulated as follows:

	Grams of Corrosion on Steel Plates Coated with		
	Zinc	*Cadmium*	*Not Coated*
Gasoline with sulfur	0.0936	0.0060	0.1126
Gasoline with sea water	0.9966	0.0250	0.1958

Write in the space below the conclusions you could reasonably draw from the results obtained in this experiment.

A practical problem is immediately encountered in collecting this evidence of achievement. The method is time-consuming. It takes considerable time for the students to formulate and write their own interpretations and usually three readers to grade the students' interpretations.

We have been developing and trying out several methods to overcome these two difficulties. The first method we tried consisted of exercises like the following.

TYPE II TEST FORM

Directions: In each of the exercises below several facts are given. After the facts, are suggested a number of inferences. Assuming these facts are true, select the inference which seems to you most reasonable and place a check mark on the blank line.

A. In an experiment some white starch was treated with brown iodine solution. This was done ten times and each time a blue color was formed.
Later some white starch was mixed with saliva. The mixture was left for a time and then treated with brown iodine solution. This was done ten times and each time no blue color was formed.

a. Saliva turns starch to sugar..... ____a.
b. Saliva turns iodine blue..... ____b.
c. Saliva produces a change in starch..... √ c.
d. The color of saliva destroys the blue color... ____d.
e. Saliva has no effect on grape sugar..... ____e.

The students are expected to select the best interpretation of those given and check it. This did not prove so satisfactory, however. When a group of students took an examination composed of a variety of experimental data and formulated their own interpretations, and immediately afterward took the new examination in which the students were expected to select the best interpretation of the same data, the two sets of results did not parallel each other closely. The relationship expressed by the coefficient of correlation was .38.

A second method was then considered. This consisted of having the students select from a list of five possible interpretations, and mark in an appropriate way, the most reasonable and most complete interpretation of the data given and the interpretation contradicted by the data given. An example of this kind of exercise is given below.

TYPE III TEST FORM

Directions: In each of the exercises below, an experiment is described. Below the description of the experiment are given several statements which have been suggested as interpretations of the experiment. Assume that the facts given in the description of the experiment are correct, then on the basis of *these facts only* select the statement which seems to you the most reasonable and most complete interpretation of these facts and place an *X* after it. Some of the statements are poor interpretations because they incompletely interpret the facts given or are partly or wholly contradicted by the facts given. Select the statement which you believe to be contradicted by the facts given and place an *O* after it.

A. Starch when treated with iodine solution gives a blue color. When saliva is mixed with the starch and left for a time the mixture no longer turns iodine solution blue.

a. Saliva and iodine do not mix..... ____a.
b. Saliva turns iodine blue..... ____b.
c. Saliva produces a change in the starch..... X c.
d. The color of saliva destroys the blue color... ____d.
e. Starch mixed with iodine solution does not turn blue..... O e.

When this method was checked with the original method in which students formulated their own interpretations, in the same way as described above, the two sets of results paralleled each other more closely.

The relationship expressed by the coefficient of correlation was .85.

A third method was thought to have further promise in that it may yield results which are still more similar to the first method and that it would show whether students can discriminate between three kinds of interpretations. Examples of this kind of exercise are as follows.

TYPE IV TEST FORM

Directions: In each of the following exercises, an experiment is described. Below the description of the experiment are several statements which have been suggested as interpretations of the experiment. Assume that the facts given in the description of the experiment, and in the results obtained, are correct, then on the basis of *these facts only* consider each statement.

Mark with a 1—every statement which is a reasonable interpretation of the results obtained.
2—every statement which might possibly be true but for which insufficient facts are given to justify the interpretation.
3—every statement which cannot be true because it is contradicted by the results obtained in the experiment.

A. In an experiment some white starch was treated with brown iodine solution. This was done ten times and each time a blue color was formed.
Later some white starch was mixed with saliva. The mixture was left for a time and then treated with brown iodine solution. This was done ten times and each time no blue color was formed.

a. The starch was changed to sugar by the action of saliva.....(2)a.
b. Saliva digested the starch.....(2)b.
c. Starch acted upon the iodine.....(1)c.
d. Saliva produced a change in the starch.....(1)d.
e. Starch mixed with iodine solution did not turn blue.....(3)e.

B. Sixty plates of the same size were cut from a piece of blue annealed tank steel. Twenty plates were coated with zinc to a thickness of 0.007 inch; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
Twenty plates were coated with cadmium to a thickness of 0.007 inch; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
Twenty plates were not coated; ten of these were placed in 200 cc. of gasoline and 25 cc. of distilled water containing 1 gram of powdered sulfur, and ten in 200 cc. of gasoline and 25 cc. of sea water.
The corrosion deposited on each of the 60 plates over a period of 7 days was carefully weighed and the results were tabulated as follows:

	Grams of Corrosion on Steel Plates Coated with		
	Zinc	*Cadmium*	*Not Coated*
Gasoline with sulfur	0.0936	0.0060	0.1126
Gasoline with sea water	0.9966	0.0250	0.1958

a. Coating the steel plates with cadmium was more effective in preventing corrosion than was coating with zinc.....(1)a.
b. In the gasoline containing sea water more corrosion was formed on the steel plates which were not coated than on the zinc-coated steel plates.....(3)b.
c. Coating pig iron with cadmium reduces the amount of corrosion formed on pig iron.....(2)c.
d. More corrosion was formed on the uncoated plates in the gasoline containing sulfur than in the gasoline containing sea water.....(3)d.
e. The distilled water corroded the coated and uncoated steel plates.....(2)e.
f. In the gasoline containing sulfur, the uncoated steel plates contained more corrosion than the zinc-coated steel plates.....(1)f.
g. It is more expensive to coat steel with cadmium than with zinc.....(2)g.

The students are expected to mark with a 1 the reasonable interpretations justified by the data given, to mark with a 2 the interpretations which might be true but are not supported by the data given, and to mark with a 3 the interpretations contradicated by the data given. Although so far as we have been able to discover, this kind of exercise did not increase the degree of correspondence with the original method in which students formulate their own interpretations, it does help to find out whether students can discriminate between three kinds of interpretations.

To those who assume that a student who has acquired a large fund of chemical information has also made the same degree of achievement in interpreting new experimental data, this work may appear to be unnecessary. We have checked that assumption. Students who have acquired a large fund of information have not always the same degree of success in interpreting new experimental data. In various fields the relationships expressed by the coefficients of correlation ranged from .27 to .60. We have also found that students who are good at memorizing facts and principles of a subject cannot always use that information with equal success in solving new problems. In various fields the relation between these two objectives ranged from .31 to .58. Likewise, students who are good at using memorized information in solving new problems are not always good at interpreting new experimental data. The relation between these two objectives ranged from .33 to .54.

The results, obtained by checking the achievement of the same students in different important objectives of teaching, indicate that in order to have a clear, comprehensive picture of the growth of students as a result of teaching, it is necessary to obtain evidence in each of the important objectives of teaching.

Philosophers may be right in affirming that we cannot transcend experience: we can, at all events, carry it a long way from its origin. We can magnify, diminish, qualify, and combine experiences, so as to render them fit for purposes entirely new. In explaining sensible phenomena, we habitually form mental images of the ultra-sensible. There are Tories even in science who regard Imagination as a faculty to be feared and avoided rather than employed. They have observed its action in weak vessels, and are unduly impressed by its disasters. But they might with equal justice point to exploded boilers as an argument against the use of steam. With accurate experiment and observation to work upon, Imagination becomes the architect of physical theory.—TYNDALL

APPLICABILITY *of the* LECTURE DEMONSTRATION METHOD *to* CERTAIN GROUPS *of* STUDENTS*

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DIFFERENCES of opinion in science are dispelled as soon as sufficient scientific data have been obtained. I need not recall any of the long list of chemical theories which have been discarded, as further studies clarified the points in question.

Laboratory investigations are not the mere accumulation of data. There are several specific steps in orderly research.

1. Can a statement of the problem be made?
2. Can any data be obtained? This takes the question out of the stage of opinions based on opinions.
3. Can the experimental variables be so controlled that the data are reasonably reliable, and are the data sufficient to average out the inherent experimental errors?
4. Can the experiments be repeated by others, thus eliminating the personal equation?

Whenever possible, differences of opinion should be subjected to the rigorous treatment of scientific research. Many of our differences of opinion are the result of our inability to submit the point in question to the scientific method.

Those of us participating in this symposium on lecture demonstration *vs.* laboratory instruction have been warned [Editorial, J. CHEM. EDUC., **12,** 152 (April, 1935)] of some of the pitfalls which we should try to avoid in our discussions.

That there exists a definite difference of opinion concerning the merits of the lecture demonstration *vs.* the laboratory method of teaching chemistry is shown by the numerous published papers on this subject. Last December, I conducted an experiment on opinions by the questionnaire method—one hundred questionnaires were evenly distributed among college chemistry teachers and industrial chemists. Among the questions were the following:

"There appears to be a tendency among some of our colleges and universities to introduce lecture-demonstration courses in beginning chemistry with the elimination of laboratory work by the student. Whom do you consider most responsible for this change? Do you believe in this method of teaching chemistry?"

The answers most frequently listed for the first question were: (1) Professors of education, (2) College administrators, and (3) Economic conditions.

In answer to the question, "Do you believe in this method of teaching chemistry?" 16% replied *Yes*, and 84%, *No*.

Such comments as the following express the opinions of both sides:

No; each chemical problem is an individual case and must be treated as such. The student realizes this only when in actual contact with the experiment.

No; *every student should have some training in the technic of some experimental science and in the scientific method. The movement probably comes from men who have had no genuine scientific training.*

No; does not train a student to do a thing himself, observe, and draw conclusions from his own observations.

No, I believe that students learn more by actually doing a thing than by seeing it done no matter how far superior to their efforts the demonstration may be. However, we should, I think, cut down on the amount of laboratory work required in general chemistry and emphasize more the type of work and the understanding of what the student is doing. Rather than sacrifice laboratory training, I believe in graduate students' teaching.

Yes; such a very small percentage of beginning students follow up chemistry; those who do not, lose the laboratory knack and knowledge gained in laboratory very quickly. Specializing students can make up the very necessary laboratory work later.

Yes; expensive laboratory work for the mass of credit-hunters is a waste of good public funds. Of course we would not give the demonstration-lecture courses alone to the real chemistry and medical students.

Even though everyone answering the questionnaire had favored one method or the other, it would not necessarily follow that the method favored is better. The only merit which this questionnaire study had was that of focusing attention on the existing difference of opinion and thereby suggesting the need for further experimentation. It appears plausible to assume that the opinions which we have are based on some evidence. We must now resubmit our evidence to the same rigorous treatment that we would apply to any other worthwhile data.

Part of the confusion concerning the merits and the applicability of these two methods of teaching rests in a failure to state the problem clearly—in what way or ways is one method superior to the other? Some have measured superiority in terms of cost of plant equipment, the size of teaching staff, immediate student interest, manipulative skill, written examina-

* Contribution to the symposium on Lecture Demonstration Method *vs.* Individual Laboratory Work conducted by the Division of Chemical Education at the eighty-ninth meeting of the American Chemical Society, New York, April 25, 1935.

tions, *et cetera*. Clearly, first and foremost in importance must be a statement of the objectives of the laboratory method. Secondly, we must consider whether or not these objectives all fall within those of the first course in general chemistry.

All teachers of general chemistry will profit by reading "Accepted objectives in the teaching of general college chemistry," by Otto M. Smith [J. CHEM. EDUC., **12**, 180–2 (1935)].

One might expect to find the objectives of the laboratory method expressed in introductions to laboratory manuals of chemistry. As a rule such communications to the students are conspicuously lacking. Preceding Experiment I there is usually a list of the experiments which may be omitted and a summary of what to do in case of accident. Such an introduction might be construed as an argument for the demonstration method. What are the objectives of the laboratory method? Obviously, all these objectives must be found among the more general objectives previously mentioned. Some of the objectives we would probably all agree upon, *e. g.*, the objectives of Professor Schlesinger:[1] to see, to think, and to do.

In the clarification of ideas on these or other objectives in the teaching of chemistry, one will find the book of E. R. Downing, "An introduction to the Teaching of Science," University of Chicago Press, **1934**, helpful. Once we have clearly stated the objectives of the laboratory method, we are in a position to attempt a comparative evaluation of the demonstration method in terms of those objectives.

In these days of forced leisure it may be that we are giving too much weight to the time factor in learning. Also, until it can be proved that one method is clearly superior to the other in satisfying the objectives of the course, cost factors should not be used as a basis for comparison. Colleges and universities will not, in the final analysis, stand or fall on the cost of education, but on their degree of success in attaining their objectives. As teachers in colleges and universities, it is not our goal to see how cheap, but how good a product we can produce—the mere granting of a degree may not be evidence of an education. If the two primary objectives to be compared are cost and the speed with which material may be processed, then it is granted that the lecture-demonstration method is superior.

TESTING THE ATTAINMENT OF THE OBJECTIVES

Having stated the objectives of the laboratory method of teaching, it is necessary to conduct the laboratory periods so that these goals may be best attained. Much of our difference of opinion concerning the applicability of these methods rests on the fact that our laboratory work is not so conducted.

If one turns to articles in the chemical research journals, one finds in nearly every article the topic "reagents" and a statement to the effect that the reagents were purified in the following manner.... The reagents, with which the data on these methods of teaching have been obtained, are human beings, which have been subjected to innumerable methods of pretreatment, and have no constants for absorbability as a function of temperature or pressure, or power of retention as a function of time.

Many attempts have been made to standardize these human errors by grouping the students according to their mental capacities, like interests, *et cetera*. Our objectives need not be the same for all groups. If the groups differ, then the applicability of the method for presenting the material may not be the same. Full cognizance of the differences in students and objectives is essential.

Harry Woodburn Chase, in the *American Mercury* for November, 1934, states that "the usual elementary courses, for example, in chemistry or biology, are taught as though each beginner were taking his first feeble step toward the Ph.D. They stress laboratory manipulation and technical detail rather than the broad underlying principles of the science as a part of the equipment of the cultured layman." It is difficult for the scientist to understand how one may teach the broad underlying principles of science and at the same time omit attention to the laboratory manipulation and the technical detail which were so essential to the development of these broad underlying principles. Is it possible so to classify chemistry students that the broad underlying principles can be taught to some, and more complete type of training given to others?

It is difficult to find published data on the exact tests used in comparing the applicability of these two methods of teaching. The tests used should be those which actually measure the degree of achievement according to the standards of the laboratory method.

Having stated the purpose of the laboratory work, these same tests must then be used by those measuring the results of the demonstration method. I cannot over-emphasize this point. Too often one reads regarding examinations, "the material used was descriptive and the tests factual." All the followers of the demonstration method must be exceedingly careful of the type of test used to measure the degree of attainment. As an example of the one specific type of test which might be used, I wish to call attention to one part of the final examination which we used at Syracuse University at the end of the first semester this year. The last three laboratory periods were used for this examination which was as follows:

The following are among the reagents which have been used this semester:

Elements—S, Sb, Al, Zn, C; *Nitrates*—$NaNO_3$, NH_4NO_3, $AgNO_3$; *Oxides*—MgO, HgO, CuO, SiO_2, I_2O_5, ZnO, P_2O_5; *Chlorates*—$NaClO_3$; *Peroxides*—BaO_2, Na_2O_2, H_2O_2; *Carbonates*—$CaCO_3$, Na_2CO_3, $NaHCO_3$; *Simple Halogen Salts*—NaCl, NH_4Cl, $CoCl_2(H_2O)_6$, $NiSO_4(H_2O)_7$, $BaCl_2(H_2O)_2$, $CaCl_2(H_2O)_6$, NaBr, NaI, $AlCl_3$, $FeCl_3$, $CuBr_2$; *Permanganates*—$KMnO_4$;

[1] H. I. SCHLESINGER, "The contribution of laboratory work to general education," J. CHEM. EDUC., **12**, 524–8 (Nov., 1935).

Sulfides—PbS; *Acetates*—$NaC_2H_3O_2(H_2O)_3$; *Acids*—HCl, H_2SO_4, HNO_3; *Sulfates*—$Na_2SO_4(H_2O)_{10}$, $CuSO_4$, $CuSO_4(H_2O)_5$, $(CaSO_4)_2H_2O$, $CaSO_4(H_2O)_2$; *Phosphates*—Na_3PO_4; *Sugar*—$C_{12}H_{22}O_{11}$; *Colloids*—$Fe(OH)_3$, As_2S_3; *Liquids*—distilled H_2O, CS_2, CCl_4, kerosene, $BiCl_3(aq.)$; *Bases*—NaOH, NH_4OH.

As part of your final examination you will be given samples of some of these materials to identify. The number of substances you examine and report upon will depend on your ability. The last three laboratory periods are allotted to this work.

1. Obtain your instructor's signature on one of these sheets, authorizing the storeroom keeper to give you a sample.
2. Take this slip and a clean, dry test-tube to the storeroom window.
3. Identify the substance given you.
4. Report to the Examining Committee (see notice on the bulletin board). If your report is correct, answer the following questions and then report again for your oral examination on this material.

(*a*) Outline on this sheet the tests used to identify the material.

(*b*) Answer on this sheet the following questions:

(1) What is the position in the periodic table of each of the elements in the substance?
(2) Show the electron arrangement of each element in the substance.
(3) Show the structural formula of the substance.
(4) List its chemical properties.
(5) Give equations to illustrate these properties.
(6) If water-soluble, show ions formed.
(7) Assuming *no* ionization, calculate the boiling point of a saturated solution.
(8) Is the substance as such found in Nature? If so, where? If not, what is a commercial method for preparing it?
(9) Uses? Cost?

Use any reference books you desire in answering these questions.

Let there be no doubt in your minds that this examination consumed a great deal of the time of my teaching staff. But I believe it was worth while. The students thoroughly enjoyed it—they learned chemistry and they benefited by the fulfilment of some of the purposes of laboratory work which I have previously outlined. What could a student trained by the demonstration method do with such an examination?

INDIVIDUAL DIFFERENCES

It has often been said that one of the favorite pastimes of college faculties is participation in curricular changes. Nearly every institution is boasting of its changes to meet the needs of the students. There is a real justification for this state of flux of our college curricula. An ever-increasing heterogeneity of student body, differences in previous training, and diversity of student interests all tend to make the stereotyped course less adaptable to the present day.

The training in fundamentals, mathematics, for example, is becoming less and less. This general factor makes it more difficult for the mediocre student to satisfy the high standards set by the science faculties. Economic conditions now make it necessary to salvage these students if possible.

One school of thought holds that our elementary science courses are not suited to the students seeking only a cultural training in the sciences. This has led in many cases to the survey type of course which is often accused of being a millimeter of physics, a smell of chemistry, a pick of geology, a peek at astronomy, a leaf of botany, a slice of zoölogy, and may even include a small proportion in mathematics and possibly a psychic bid or two. From this viewpoint, the problem stated briefly is, which is better—a blind spot or a blur?

Next fall (1935), Syracuse University inaugurates a course in the physical sciences and a course in the natural sciences. These two courses will satisfy the science group requirement. To take care of individual student differences, the student can substitute an equivalent number of hours in the regular laboratory courses in either physics or chemistry; or geology, botany, or zoölogy. In these new courses the lecture demonstration will play an important part. It appears to me that the greatest applicability of this method rests in courses of this type.

In the questionnaire already mentioned, this question was asked: "Do you believe if a student is to take only one course in the physical sciences that, on the average, it will be more valuable for the student to take one course in one science than a composite course, for example, in astronomy, chemistry, and physics?" Forty-seven per cent. of the replies said *Yes* and 53% said *No*. Some of the comments added are interesting:

No; a single course in science should be built around a few broad generalizations of science, the mastery of which will enable the layman to appreciate science and scientists.

No; a student not majoring in science should take a composite course, the so-called general science course.

Yes; if he can take but one science, let him concentrate on one rather than portions of several.

Yes; there is a definite place for a survey course in high school, not in college.

These students come to our chemistry classes in most cases because a science is required. They have chosen chemistry as the lesser of two evils (usually the choice is physics or chemistry). They have an abhorrence for the smells of the laboratory, a fear of the popping of hydrogen, and a dislike for washing test-tubes. If one studies their cases carefully, it will usually be found that their blind spot is the lack of ability to do anything for themselves which calls for persistence, accuracy, and organization. The changing curriculum is evidence that our present courses are not adaptable to these students. If they are taught by the demonstration method they can at least see science in action. The cultural value of science will be emphasized. Whether or not the students have more than a blur at the conclusion of such courses will depend upon the teachers, their objectives, and standards of achievement. To some it appears better that we realize that we are dealing with an inferior type of science student and give them that which they are capable of mastering, rather than attempt to force them beyond their capacities.

Much of our whole educational program, within and without schools, tends to educate by methods which

make no provision for "doing." Unless at the same time we at least give the student an opportunity to learn by doing, our practice may be the curse of future generations. May I offer the plea that we give the student an opportunity for individual expression of preference as to the type of training he is to receive and that if he wants to work in the laboratory, he may be permitted to do so? Never in the history of this nation has there been greater need for power of individual observation and critical analysis.

Having dealt with the poor student, we must consider the good students and the students interested in science. Scientific technic comes from experience—there is a definite carry-over from one field of science to another. The laboratory offers the best opportunity for individual expression of these students and it is here that we can truly accommodate individual differences among students.

In the second semester of the 1933–34 school year, we segregated our "A" students and then carried out four experiments by the demonstration method, four experiments with students working in groups of four, and four experiments with students working in pairs, and then asked the students how they wanted the laboratory operated for the rest of the time. They were almost unanimously in favor of the individual laboratory method which they had used during the first semester, as this method gave them the most freedom for individual work.

CONCLUSIONS

In view of the financial pressure upon schools at the present time, it is advisable that these experiments be extended until they prove to the satisfaction of the college and school administrators and teachers the relative merits of the lecture-demonstration and the laboratory method. These experiments must follow the orderly course of any other scientific investigation.

We need to have clearly in mind the objectives of general chemistry and the objectives of the laboratory method.

Examinations must test the degree of achievement of these objectives.

The lecture-demonstration method is most applicable to students whose major interests are not in the sciences.

A middle ground upon which teachers can stand is to offer both types of courses. The results of years of experience will serve as the true guide and justification for the survival of the fittest. The student would at the same time be assuming the responsibility for the type of science training he is to receive, which places the responsibility where it belongs in college education.

A CHAPTER *in* TEACHING ACIDS, BASES, *and* SALTS*

P. M. GLASOE

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ONE of the chief complaints that can be directed at our first-year chemistry teaching is that of lack of systematic arrangement of the subject matter. We teach by chapters and all too often there is no connection shown—in fact, too frequently there is none. Each chapter becomes a separate memory task; there are no starting points from which the subject matter may be developed nor around which the facts may be organized. For example, what connection, relation, or sequence can be conjured up between a chapter on "Carbon and its Oxides" following a chapter on "Water and Hydrogen Peroxide," and followed in turn by one on "The Halogens and their Acids"? The discussion of carbon and its oxides does not follow water and hydrogen peroxide by any other right or reason than that it had to come somewhere, so it might as well come here. Each chapter becomes a separate pigeon hole of facts and the test that follows can be nothing but a test of sheer memory—and that is not necessarily chemistry.

It is no wonder that a contributor to THIS JOURNAL[1] found that in the case of a total of 1292 sets of responses to College Entrance Examinations ninety per cent. of the mental effort required was memorization. This is consistent and inherent in the situation, for several reasons. Altogether too many teachers are young and inexperienced; memory exercises are easily assigned, easily checked up, easily put to the student, and most easily scored in tests. Then, too, memory questions are by far the easiest to make out. None of which justifies making first-year chemistry a ninety per cent. memory course.

"It is no wonder schools for concentration and other

* Presented at the eighty-ninth meeting of the American Chemical Society before the Division of Chemical Education, New York, April 26, 1935.

[1] RICH, STEPHEN G., "Mental processes required in examinations in chemistry," J. CHEM. EDUC., 3, 445–9 (April, 1926).

examination-passing schools have for years past operated with success on the assumption that memory work alone could insure a pass."[2]

The present writer once listened to two young chemistry teachers roundly upbraiding the teaching in some 150 high schools to which their set of a hundred or more questions, covering the whole year of chemistry, had been submitted. The set of questions was a typical memory test, and the results were, according to these surveyors, a sad demonstration of the kind of chemistry teaching prevalent in the high schools.

In passing let me ask: who is to blame for this lamentable condition? The universities and colleges prepare the high-school teachers—when there is better teaching in these higher institutions there will be better-trained teachers sent out into the high schools. The writer has previously called attention, in THIS JOURNAL,[3] to the fact that college teaching of today is only high-school teaching "grown up," and when university students go out to teach they naturally teach college chemistry "grown down" to the level of high-school children.

I am going to make so bold as to try to show how a certain chapter of chemistry can be taught logically, systematically, and with a maximum of thinking operations. The subject of the chapter is "Acid, Base and Salt." Judging by the textbooks in my possession this most important generalization of first-year chemistry gets scant attention. Acid and acidity are taught in one chapter, base and basicity in another, and neutralization in still another. There are literally hundreds of facts that spring from these considerations and without an organizing thread running through it all the pupil becomes hopelessly swamped. In this presentation no claim is made to novelty of subject matter; it is the method of presentation to which attention is invited. It must be possible to present a subject, so vital to the first-year student, in such a way that the facts follow in natural sequence, making it possible for the student to reason his way instead of simply memorizing a mass of names and formulas. The writer would call it Nature's way of presenting the subject.

When we set about studying the map of the world we do not begin by learning the names of the ninety-two largest cities alphabetically with no reference to the map; we study them according to their position and relation to the hemispheres, the continents and countries, and sometimes even the smaller subdivisions of the latter, the states. Should we assign the task alphabetically it would be fair to expect results, but it would be memory work pure and simple. On the other hand, if we require them to be learned by countries there are innumerable relations cropping up which so grip the mind that the names, common language, populations, customs, industries, institutions of learning, and much else will naturally group themselves about and interrelate them. In what are they similar? In what different? What do the similarities lead to? And the differences?

Nature furnishes us a map for the study of acids, bases, and salts. Here is a part of it—all that is necessary for first-year chemistry.

I	*II*	*III*	*IV*	*V*	*VI*	*VII*	
Li	Be	B	C	N	O	F	(Ne)
Na	Mg	Al	Si	P	S	Cl	(A)

This study does not need to be postponed to the tenth or fifteenth chapter of a textbook. Even high-school pupils know the name of every member of the sodium-magnesium series and one of the prime principles of pedagogy is to build on the information the pupils already have. It lends human interest and dignity to the subject for the student to find that he can contribute something from his own experience.

Every college freshman or high-school chemistry student knows about vinegar, sour milk, muriatic acid (tinner's liquid), sulfuric acid (battery fluid), oxalic acid (rust-spot remover), orange and lemon juices, and fruit juices in general. All these have the common characteristic of sourness. They already have learned that sour substances are called acids. Likewise they know about soda (sal and baking), ammonia (cleaning fluid), lime water and milk of magnesia (antidotes for sour stomach), lye (soda and potash), borax (water softener), etc. If they do not already know it they are now told that these substances are called bases or have a basic nature. All this is their stock in trade; it is unorganized, therefore not yet science. They have entered the chemistry class in order that this may be systematized for them.

Most intelligent young people know about neutralization but not by that name. The women know about "sweetening" sour milk with soda, the boys know that the tinner "cuts" his muriatic acid with zinc. They all know that milk of magnesia counteracts a sour stomach. They have registered for chemistry and are about to learn the reason for the "sweetening" and the "cutting" and the "counteracting."

You may ask, how early do you expect to introduce this chapter? I answer, very early. Everyone knows that sodium, magnesium, and aluminum are *metals*. As we approach the right end of the series—*the opposite end*—we no longer recognize the elements as metals, and so we very naturally call them *non-metals*. That is reasonable—it appeals—the positions are opposite; so are the properties. No elaborate foundation is necessary for the study—it is simple, reasonable, *natural*. By an elementary electrolysis demonstration it may be shown that metals are positive—go to the negative pole; non-metals are negative. Chlorine may be liberated right before the students' eyes—at the positive pole. So far our map looks like this:

Na Mg Al	Si P S Cl
← Metals →	← Non-metals →
Positive	Negative

[2] RICH, *loc. cit.*

[3] GLASOE, P. M., "The deadly parallel between high-school and college chemistry," J. CHEM. EDUC., **6**, 505–9 (March, 1929).

Drop a piece of sodium on water: it hisses as it floats around and if a burning match be brought near it a yellow flame plays over the metallic globule. A piece of red litmus paper dropped into the beaker turns bright blue, which it will not do in pure water. If the water be evaporated a white crust is obtained which has the same properties as the soda lye which may be bought at the corner grocery under the name Lewis lye. The metal sodium has been turned into lye. If you collect the gas given off in a test-tube it may be identified as hydrogen; it was the hydrogen that burned, not the sodium. The yellow flame was due to the characteristic sodium influence. The substance made was NaOH, our first base, obtained from the first metal of the second short series.

While the first three elements are positive and the last four are negative in electrolysis, we find that positive valences persist clear through the series. The fact that multiple valences appear may be shown by the following summary:

Group	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*
Valences	+1	+2	+3	±4	+5	+6	+7
					±3	+4	+5
						±2	+3
							±1

Magnesium will duplicate the behavior of sodium but in a much weaker degree. The product obtained is $Mg(OH)_2$ and it turns litmus paper faintly blue. Magnesium and water react on each other so slowly that you might boil a piece of magnesium for hours without noting any decided change, but the water is found to be faintly basic. $Mg(OH)_2$ can be easily made by other methods: the important thing here is that there is such a compound and *that it is a base.* The student next has his attention drawn to the fact that aluminum and water have apparently no affinity for each other. In fact he knows this in advance: the universal use of aluminum cooking utensils supports the conclusion. However, aluminum foil or powder are very slowly converted to $Al(OH)_3$ when boiled with water. The hydroxide is insoluble and has no influence on litmus paper. If, now, it be recalled that Na, Mg, Al, succeed each other in that order because their atomic weights are 23, 24, 27, it becomes nothing short of astonishing to find that their hydroxides vary from the strongest corrosively basic, soda lye, NaOH, through $Mg(OH)_2$, a weak and indifferent base, to $Al(OH)_3$, so weak that the ordinary litmus reaction fails to respond to it; we have to resort to other means to identify it as a base. Here is a sequence which is sufficiently surprising and interesting to help fix the whole thing in mind. Had it been learned in three separate, nonrelated chapters, the fact of this gradation of basic property might never have come home to the student at all. We are now through with the bases of this series. When you come to follow up the study it is possible to say that what we have found out about sodium will be duplicated in the case of potassium and the student can be led to predict what might happen in case of Li, Rb, and Cs. Likewise what we have learned about Mg will be found to be true about Ca, Sr, and Ba, with modifications that inhere in their positions.

Going on to Si, we find the hydroxide $Si(OH)_4$. The student having followed our succession of hydroxides so far is not surprised to learn that this hydroxide has not a trace of basic property; on the other hand, it may be recognized instead as a very weak acid. As an acid we write it H_4SiO_4. It is not only weak as an acid, it is so unstable that upon exposure to the air it loses a molecule of water and becomes H_2SiO_3. By way of comparison again it may be brought out here that NaOH is so stable—resists decomposition to such an extent—that it requires the temperature of molten cast iron to break it down, while $Mg(OH)_2$ loses a molecule of water at moderate red heat, $Al(OH)_3$ breaks up at low red heat, and H_4SiO_4 loses water spontaneously at room temperature.

Having said this much the student is already anticipating the statement that the hydroxide $P(OH)_5$ does not exist. However, its immediate derivative H_3PO_4 does exist and is known as phosphoric acid. True to its position, this acid is decidedly stronger than H_4SiO_4, sufficiently strong to show the typical acid influence on litmus paper.

Sulfur is the next element in order and should give the hydroxide $S(OH)_6$. This is not known in the free state, but there is proof of its existence in solution. We know its derivative, $S(OH)_6 - 2H_2O$, as sulfuric acid, H_2SO_4, and this is very much stronger as an acid than the foregoing, H_3PO_4. Arrhenius states that of all the hydrates of sulfuric acid for which claims have been made he found evidence of but two: $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 2H_2O$. The latter may well be $S(OH)_6$ and the former $S(OH)_6 - H_2O$.

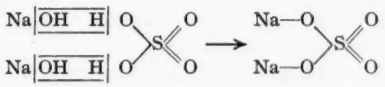
Only chlorine, of Group VII, remains to be treated in this series. To be true to its position it ought to produce an acid derived from the parent hydroxide, $Cl(OH)_7$, and so it does. Removal of three molecules of water gives rise to $HClO_4$, the strongest acid in the series. On the basis of the hydroxides and their derivatives our map now looks as follows:

I	*II*	*III*	*IV*	*V*	*VI*	*VII*
$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$ $-H_2O$	$S(OH)_6$ $-2H_2O$	$Cl(OH)_7$ $-3H_2O$
			↓	↓	↓	↓
Very caustic base	Weak base	Very weak base	H_4SiO_4 Very weak acid	H_3PO_4 Considerably stronger acid	H_2SO_4 Strong acid	$HClO_4$ Very strong acid

From a previous study of these seven elements it has been brought out that since the strongest positive property is found in Group I and the strongest negative in Group VII it follows logically that Na and Cl will combine with the greatest avidity; the affinity of Mg for Cl is somewhat weaker, and Al is still weaker in its action. By the same reasoning Na and S will unite less vigorously than Na and Cl; Na and P will unite but not with the display of energy of the other combinations. Na and Si have never been made to combine directly. Since there is a consistent variation in the

affinity shown, the student is in a position to predict in advance, not only which elements will combine, but the degree of chemical affinity and the stability of the compounds.

In view of the fact that opposites attract, as shown by the union of Na and Cl, it is a plausible conclusion that bases and acids will unite, being from opposite ends of the series. A trial, using two of the compounds already derived, NaOH and H_2SO_4, H_3PO_4, or better still, $HClO_4$, shows at once the correctness of the deduction. While NaOH turns litmus strongly blue and H_2SO_4 turns it strongly red, a mixture of the two may be made which is neutral to litmus. Both the base and the acid have been neutralized. Since all bases are hydroxides of metals and all acids are hydroxides of non-metals, the neutralization process can best be shown thus:



If the water is evaporated a white residue of Na_2SO_4 is left. Here is plenty of chance for thinking and reasoning. Showing the combination of the three bases with the four acids, as worked out above, gives opportunity for twelve distinct neutralizations.

But what about the acids derived by use of other valences of the non-metals? Care is necessary not to introduce so many new things as to confuse the student. But gradually the subject of the influence of multiple valences may be taken up. Silicon has only one valence, but there are two acids possible and therefore the designations ortho- and meta- must be introduced. Thus H_4SiO_4 is ortho-silicic acid and when H_2O is lost we have H_2SiO_3 or meta-silicic. Phosphorus of Group V gives the first illustration of the effect of multiple valence. Phosphorus has two valences, ± 3 and $+5$. We have already derived the acid H_3PO_4, but since it is possible to subtract a molecule of water and still have an acid remaining, it is necessary again to resort to the ortho- and meta- designations. With a valence of three, P should form a hydroxide $P(OH)_3$, which it does. This exists without the loss of water as orthophosphorous acid, H_3PO_3. By inspection it is apparent that by loss of water metaphosphorous acid is produced. This is the first place where it becomes necessary to use the distinctions -ic and -ous in identifying acids. We note that there are two acids of pentavalent P, called phosphoric acids, and two of trivalent P, called phosphorous acids.

PHOSPHORUS—PARENT HYDROXIDES AND DERIVATIVES

5-valent Phosphorus (-ic) $P(OH)_5$		3-valent Phosphorus (-ous) $P(OH)_3$	
Acids		*Acids*	
H_3PO_4 Orthophosphoric Acid	HPO_3 Metaphosphoric Acid	H_3PO_3 Orthophosphorous Acid	HPO_2 Metaphosphorous Acid
Salts			
Orthophosphates	Metaphosphates	Orthophosphites	Metaphosphites

We have to treat sulfur in the same way. Being in Group VI it should show valences of ± 2, $+4$, and $+6$. In reality it shows acid tendencies only with $+4$ and $+6$.

SULFUR—PARENT HYDROXIDES AND DERIVATIVES

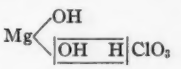
+6-valent Sulfur (-ic)	+4-valent Sulfur (-ous)	+2-valent Sulfur
$S(OH)_6$-$2H_2O$	$S(OH)_4$-H_2O	$S(OH)_2$
H_2SO_4	H_2SO_3	No acid derivative from this hydroxide

The acids derived from chlorine with valences of $+1$, $+3$, $+5$, and $+7$ are easily taught.

CHLORINE—PARENT HYDROXIDES AND DERIVATIVES

+7-valent Chlorine	+5-valent Chlorine	+3-valent Chlorine	+1-valent Chlorine
$Cl(OH)_7$-$3H_2O$	$Cl(OH)_5$-$2H_2O$	$Cl(OH)_3$-H_2O	Cl(OH)
Perchloric Acid	Chloric Acid	Chlorous Acid	Hypochlorous Acid

We have now reasoned our way to twelve different acids: two for Si, four for P, two for S, and four for Cl. This gives an abundance of chance for neutralization. Every case must be reasoned out on the basis of the number of hydroxyl groups in the base and the number of hydrogens in the acids. Right here is a good time to bring in acid and basic salts. Taking a simple case:



yields $Mg(OH)ClO_3$, basic magnesium chlorate. $Al(OH)_3$ can give three kinds of salts with $HClO_3$: $Al(OH)_2ClO_3$, $Al(OH)(ClO_3)_2$, and $Al(ClO_3)_3$. In like manner the student can be taught to develop the acid-salts. Thus: three sodium phosphates, three sodium phosphites, etc. Until students have mastered such equations and can write six possible sodium silicates, four possible sodium phosphates, four sodium phosphites, two sodium sulfates, two sodium sulfites, and four sodium salts of the chlorine acids, giving the correct name of each salt, they have not mastered the mechanics of neutralization equations. It should give a pleasant thrill to a student to be able to predict theoretically the existence of twenty-two sodium salts in the second short series of the Periodic System. This may be followed up by using $Mg(OH)_2$ as the base, and then $Al(OH)_3$. These series of neutralization derivatives are full of interesting problems. Why are both $AlPO_4$ and $Al(PO_3)_3$ aluminum phosphates? Why are $Mg_3(PO_3)_2$ and $Mg(PO_2)_2$ both magnesium phosphites? How can there be three perchlorates of aluminum?

Numerous questions requiring reasoning and hard thinking can be asked in connection with this method of procedure. If it is reasoning we want to teach instead of mere memory work, we must resort to some such systematic method of presentation. A year of memory work in high-school chemistry soon goes the way of all unused facts. There is no use in trying to make an encyclopedia of memorized facts out of every student that comes to us; if we succeed in giving them even ever so few starting points to tie to we shall have done them a great service. Let us teach thinking and reasoning—let memory work be a means to an end, not an end in itself.

A PLAN *for the* OPEN HOUSE *in* CHEMISTRY

AMY LE VESCONTE

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The simplest of experiments performed by enthusiastic students will interest visitors more than elaborate displays of apparatus or chemicals. The students, themselves, learn much from their demonstrations and from the thought-provoking questions of the visitors, and their interest in the subject is deepened.

✦ ✦ ✦ ✦ ✦ ✦

AN OPEN house in the science department offers an opportunity to the students to demonstrate the technic and ability they have developed in their laboratory work. It also gives students who do not study science a chance to see what takes place in a laboratory, and by interesting these students it may bring about a substantial increase in science enrolment the following term.

At Mary Hardin-Baylor, a liberal arts college for girls, the chemistry department holds an open house near the close of each fall term. A few weeks before the date, students with artistic talent are enlisted to make posters of chemical apparatus or symbols to announce the event. Usually over half of the student body and faculty from the college find it possible to attend, and spend from thirty minutes to two hours studying the exhibits and demonstrations throughout the three laboratories. To make the laboratory more festive, flowers in season are interspersed with the exhibits. These are arranged in flasks, beakers, casseroles, and evaporating dishes. One of the most effective of these flower arrangements is a single bud in a volumetric flask, with leaves immersed in the water, which is tinted with eosin.

Every student enrolled in chemistry, even in the beginning classes, is asked to assist in the open house. Some of these meet the guests as they arrive, and usher them through the laboratories in a definite order, thus avoiding confusion. The more capable students prepare and demonstrate one or more of the experiments. Usually two or more students are assigned to each desk to perform the experiments or to explain the significance of the exhibits placed there. This makes it possible for them to relieve each other to visit the other laboratories. The students enjoy the responsibility that is given them, and respond by taking an active interest in making the occasion a success. They make many helpful suggestions and arrange the final details of the experiments with much care. This interest is contagious, and the visitors are affected by it as soon as they start their tour of the laboratories. Probably the success of any demonstration depends more on the enthusiasm of the student who explains it than on the excellence of its preparation. It should be added, however, that at each exhibit a typewritten explanation is placed, since occasionally students desert their assignments. Only the most interested and conscientious observer will read these, while a visitor must be very uninterested to be able to pass by an enthusiastic student without hearing a full explanation.

It has been found advisable to alternate demonstrations that have a definite practical application showing the useful side of chemistry, with a few very simple experiments on the theory of chemistry, such as the electrolysis of water, and with several experiments for entertainment only, showing the side of chemistry that is "fun."

These open house events have revealed a most surprising interest, on the part of casual visitors, in extremely simple demonstrations. A freshman bending glass tubing and blowing small glass bulbs always has an admiring audience. Many of the guests take unusual pieces of glass with them as souvenirs. Moreover, students who demonstrate glass blowing usually develop their technic considerably during the two hours of the exhibit.

Writing with chemicals is always simple to explain and effective in creating interest. As they arrive, the guests register in a book made of yellow paper, the pages of which have been sponged with potassium thiocyanate, potassium ferrocyanide, or potassium ferricyanide, and dried. Although all the pages look alike to the casual observer, when a solution of ferric chloride is used as ink the writing may appear either as red, blue, or green. A most popular souvenir is a piece of white paper coated with colorless phenolphthalein, and cut in the shape of an Erlenmeyer flask. Students enjoy seeing the red appear when they write on these with sodium hydroxide.

Other entertaining features are found throughout the laboratory. The "educated moth balls," fire-writing, and chemical flower gardens are familiar (*1*), (*2*). One demonstration that furnishes entertainment through the laboratories is "chemical music," a group of beakers, tuned by varying the amounts of water in them and arranged in order to play a favorite melody when tapped with a glass rod.

Interspersed with the experiments in action are exhibits of work that have taken more time to prepare. "Chemical jewels" include huge crystals of copper sul-

fate and alum (*3*) and various crowns and baskets of potassium dichromate (*4*) prepared as optional experiments by students. Lead trees (*5*) are often on display, and "depression gardens" (*6*) add color to the laboratory tables.

Among the more practical exhibits are demonstrations of methods of distinguishing cotton and rayon from wool and silk, or the methods of purifying and softening water, or the action of baking powders. Crystals of potassium permanganate dropped into a beaker of water and then heated show convection currents in the form of pink streaks through the water. A model of a sulfur mine is especially interesting to people in Texas (*7*). Meat, flowers, and mercury are frozen with dry ice. The steps in making the four types of rayon are demonstrated by an advanced student.

In all these demonstrations, the explanations are made as complete as possible, without the use of scientific terms, and the possibility of making a practical application of the knowledge is stressed.

Many girls think that chemistry is useful if they can learn something about cosmetics. Tooth paste, finger-nail polish, cold creams, and hand lotions made in the laboratory are on display, with a student to demonstrate them. Some of the favorite formulas are:

Vanishing Cream

Mix equal parts by weight of calcium carbonate and zinc stearate in a casserole. Add glycerin, diluted with an equal amount of water, to the desired consistency. Add perfume and color as desired.

Vanishing Cream

Heat 100 grams of stearic acid to 80°C. In a separate beaker mix 1.5 grams of potassium carbonate, 35 grams of glycerin, and 300 cc. of water. Heat this mixture to 80°C. Add to the melted stearic acid, stirring rapidly until thick. Stir in perfume as desired. Let stand a few days, stirring occasionally.

Cold Cream

Mix equal parts by weight of spermaceti, white beeswax, and lanolin and melt in a quantity of mineral oil equal to the combined weights of the solids. Heat to 80°C. For each 15 grams of oil, add a gram of borax dissolved in 15 cc. of water, heated to the same temperature. Stir until cool.

Hand Lotion

Soak 4 grams of gum tragacanth in 300 cc. of distilled water overnight. Beat with an egg beater until smooth. Add 25 cc. glycerin, 15 cc. alcohol, and perfume and color as desired.

Finger-nail Polish

Dissolve pyroxylin in "banana oil" to give the desired consistency. Color with eosin.

Tooth Paste

Mix equal parts by weight of powdered Castile soap, talc, and sugar with precipitated chalk equal to the combined weight. Add glycerin, diluted with an equal volume of water, to make a paste. Add oil of peppermint and menthol to taste.

The nature of many cosmetic frauds and reducing mixtures is made more vivid by posters and exhibits, and many students are thereby enlightened.

One display that always attracts interest is the "chemical girl," a group of fairly well-known substances which added together would have approximately the same percentage composition as the human body. The name is derived from the placard that states that when mixed properly, the materials would make a one-hundred-pound girl. The substances used are:

Coal	20.2 lb.
Water	61 lb.
Ammonium hydroxide (conc.)	5.47 lb.
Calcium fluoride	133 grams
Phosphorus	518 grams
Sodium chloride	118 grams
Sulfur	64 grams
Magnesium ribbon	32 grams
Iron nails	4.5 grams
Potassium hydroxide	72 grams
Iodine	18 milligrams

The advanced classes in chemistry prepare some more impressive demonstrations, such as the making of ether, carbolic acid, or a coal-tar dye. The classes in analytical chemistry attempt to explain the importance of their work by demonstrating typical experiments. These, however, usually receive less attention than the simpler and more entertaining exhibits.

As a fitting climax to the open house, the guests are invited to a chemistry tea table, set with filter paper for doilies, flasks for candle sticks, and an evaporating dish for flowers. Glass tubes are used for tea sippers. At each end of the table 5-liter flasks of tea are siphoned into beakers. The sandwiches and cookies cut in the shape of chemical apparatus are served on large watch glasses. One year the home-economics department coöperated by making baking-powder biscuits using concentrated hydrochloric acid, a possibility that was explained by an exhibit in the laboratory.

The open house is considered a success when the visitors who attend it say that they have not only enjoyed the exhibits, but also have learned something worth while. Student visitors learn that chemistry has many useful applications and that it can be interesting. The students in the department develop so much interest and enthusiasm in assisting with the demonstrations that this result alone would justify the effort and work required. It is the hope of the author that other teachers may find some suggestions in this article to make their own open-house exhibits a greater success.

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PROFICIENCY *of* FIRST-YEAR STUDENTS *in* QUANTITATIVE EXPERIMENTS

BRUCE S. FARQUHAR WITH FRANCIS EARL RAY

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SINCE Herbert Spencer published his famous essays on education, the battle has raged over "What knowledge is of most worth." Without venturing into the general topic, we would submit that what is done must be well done if it is to accomplish any of the advertised objectives. The progress of civilization has been marked by the steps taken to establish standards of value. In the last two decades the "standard test" has been introduced into our educational system as an aid in comparing the work in different institutions. While an examination into the merits and demerits of the standard test is beyond the scope of this brief note, it will be obvious that a "standard test" can give no information in regard to the proficiency attained in laboratory technic. It was, therefore, with the idea of encouraging the establishment of norms for laboratory performance that we undertook a detailed analysis of the achievements of students in our beginning laboratory course in chemistry.

EXPERIMENTAL DATA*

Comparison of grades is not very informative, for a grade is often a better indication of the metabolism of the grader than it is of the quality of work done by the gradee. We selected, rather, the actual figures obtained by undergraduates in quantitative experiments. The results we present, while limited in scope, are universally comparable. It is hoped that others will publish their data so that standards of achievement may be available for all quantitative experiments.

Synthesis of Cuprous Sulfide. (Figure 1.) This is the usual experiment in which a weighed amount of copper is heated with an excess of sulfur. All weighings were made with horn-pan balances. We have tried beam balances but the cost of these made it necessary to assign several undergraduates to each balance. The attendant confusion and loss of time led us to abandon the practice. The results with horn-pan balances compare favorably with those obtained with beam balances. The limiting factor seems to be the manipulative skill of the student rather than the sensitivity of the balance.

Figure 1 shows the distribution curve. The percentage of copper reported is plotted against the number of students reporting this percentage and a smoothed curve drawn. The theoretical percentage is 79.9. Of 160 students all but three came within 10% of the correct value, as shown by the solid vertical lines. The dotted lines show that 50% of the class came within the values 76–81%. The error, it will be observed, is much greater on the low side of the theoretical value, showing that the excess sulfur was not always completely burned.

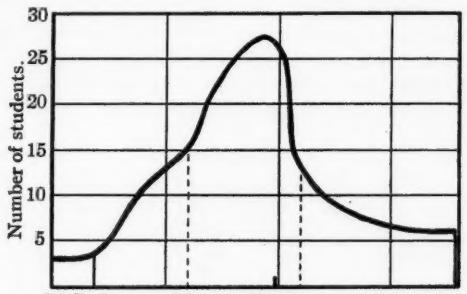

FIGURE 1.—PER CENT. COPPER IN CUPROUS SULFIDE

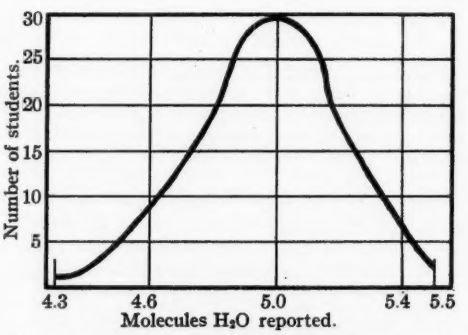

FIGURE 2.—MOLECULES H_2O IN HYDRATED COPPER SULFATE

Water of Hydration of Copper Sulfate. (Figure 2.) In this experiment a weighed amount of copper sulfate is heated to constant weight. As there are five molecules of water in blue vitriol, any value below 4.6 or above 5.4 would have no significance. Only five students in 160 failed to come within this limit. As Figure 2 shows, the majority came much closer than

* Complete details of each experiment will be found in "Experimental chemistry," by F. E. RAY (J. B. Lippincott Co.).

this. Thirty-four, or 21%, failed to come within the limits 4.8–5.2, which represents a four per cent. error. The curve also shows that overheating of the sample is about as common as underheating.

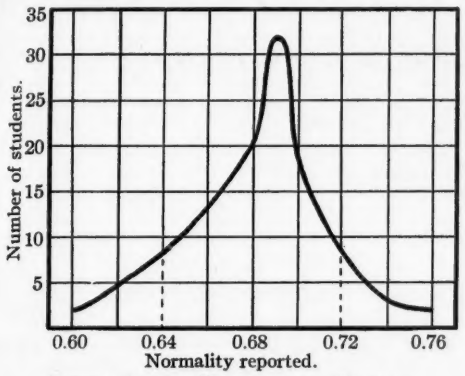

FIGURE 3.—THE NORMALITY OF VINEGAR

The Normality of Vinegar. (Figure 3.) The alkali is standardized by titrating it against standard (0.25 *N*) acid. The vinegar is then titrated and its normality calculated. Allowing a spread of from 0.64 to 0.72, which is about 6%, we find that only two students exceeded this range, while 13 fell below. Ninety per cent. of the class might thus be considered as doing acceptable work. The maximum of the curve is to the right of the correct normality. This is somewhat remarkable in view of the fact that the greatest deviation is to the left. One might infer that the careful student tended to get slightly high results while the careless person reported results much too low.

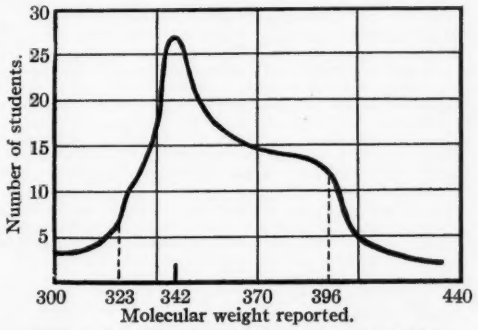

FIGURE 4.—MOLECULAR WEIGHT OF SUCROSE

Molecular Weight of Sucrose. (Figure 4.) A weighed amount of sugar is mixed with cracked ice and the temperature is recorded. The solution is decanted and the weight of sugar and water obtained. The temperature lowering is about five degrees. The error in taking the temperature alone is close to 10%. It is, therefore, somewhat surprising that over 80% of the students came within 10% of the correct value, 342. Of a class of 160, 93% came within 15% and 98% came within 20% of the correct value. The chart (Figure 4) shows that the error was mostly on the high side. Failure to reach the true equilibrium temperature was, no doubt, the cause of this. Values between 323 and 393 were considered acceptable. This covered 85% of the class.

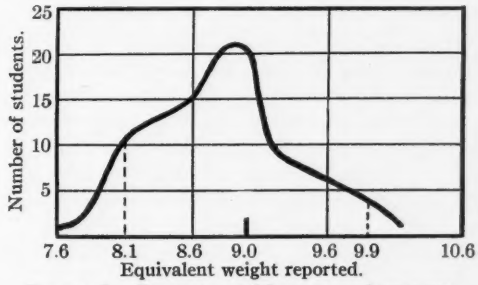

FIGURE 5.—EQUIVALENT WEIGHT OF ALUMINUM

Equivalent Weight of Aluminum. (Figure 5.) This determination is made by measuring the volume of hydrogen liberated by dissolving a weighed amount of aluminum wire in acid. Loss of gas should be the source of greatest error. It is, therefore, quite remarkable that Figure 5 shows that most of the values were on the low side. The only explanation that can be advanced at present is that the heat of solution of the metal in acid caused a portion of the gas to occupy a larger volume than it normally would. This hypothesis will be tested out in subsequent classes. If an error of 10% is assumed to represent the limits of creditable work, we find that 14 of 154 students reported values below 8.1 for the equivalent weight. Eleven students reported values above 9.9. This means that 16% of the class failed to come within 10% of the correct value. This percentage, singularly enough, coincides almost exactly with the percentage of undergraduates failing the course.

It is the authors' belief that if many similar data could be collected from colleges all over the country a valuable contribution would be made to chemical education.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE ANIONS—CORRECTIONS

Page 586 (Dec., 1935), under GROUP I, Ions: include *sulfite.*

Page 588, under *Group VI—Detailed Analysis, Preparation of solution for nitrate test:* read *barium acetate* for "barium nitrate."

BIBLIOGRAPHY *for* GENERAL CHEMISTRY *from* SEVERAL PERIODICALS*

I.† CHEMICAL AND METALLURGICAL ENGINEERING‡

Volume **1** *(1902) through* **41** *(1934)*

HUBERT N. ALYEA

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IT IS amazing that so many articles in our technical journals may be intelligently read by students who have had practically no chemistry; but such is the case for those articles in the following bibliography which has been developed at Princeton for reference work in original literature. This encourages individualism, offers contact with methods of research, and, because of the latitude of subjects from which the student is free to choose, has been one of our most stimulating projects.

The responsibility of abstracting one of these articles replaces a certain amount of pedantic drudgery in rewriting experiments performed in the laboratory; and it amplifies the "independent reading" prescribed for those taking a course in chemistry without laboratory work.

The bibliography has not been compiled by referring to the indices, but by a careful paging of each volume. Processes which are obsolete, such as the arc process for nitrogen fixation, have been omitted. The following items are recorded for each article. *Number* (best articles starred), *title, author, periodical, volume, inclusive pages,* and *year. Sub-titles;* a detailed abstract of the contents of the article. *Pictures* (photographs), *figures* (diagrams of apparatus), *graphs,* etc.; from which the type of article may often be inferred. *The author's estimate of the article.* This is catalogd, for uniformity, under the headings:

POPULAR	CHEMICAL	ENGINEERING
Historical	Equations	Equipment design
Raw materials	Research	
Processes	Advanced	
Products	Mathematics	
Properties	Organic required	
Economics	Biological	
No organic required		
Little chemistry		

Only the general approach classifies the article; thus mere reference to one or two previous workers in the field would not qualify it as "historical." The absence of any one of these headings indicates that such material is lacking. *Reading time,* estimated from the amount of printed matter; no attempt being made to approximate the time it would take a student to abstract the article. Very short articles have been omitted, since this bibliography proposes, in so far as is reasonable, to supply the student with references involving approximately two hours' work. In the case of brief articles two may be assigned.

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***1. Pioneers of electrochemistry.** *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), **1,** 10 (1902).—Charles M. Hall; 56, Cowles; 90–1, Acheson; 121, Castner; 214–5, Ostwald; 451–2, Bradley. Also *ibid.*, **2,** 103 (1904).—Edison. 7 portraits. *Popular: historical, economics, research. 2 hrs.*

***2. Low temperature researches.** DEWAR. *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), Part I: **1,** 91–6 (1902).—Liquefaction of gases, continuity of state, liquid hydrogen, and helium. *Chemical: historical, research. 1 hr. 50 min.* Part II: *ibid.*, 137–40. —Attempts to reach absolute zero; liquid helium. *Chemical: research, advanced. 1 hr. 15 min.*

3. Aluminum as a reducing agent in metallurgy. SCHOLL. *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), **1,** 175–8 (1903).—Thermochemistry of Goldschmidt process; use in producing manganese, ferrotitanium, rail-welding. 6 pictures, 1 figure. *Chemical: research, advanced, theoretical. 1 hr.*

4. Aluminothermics. GOLDSCHMIDT. *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), **1,** 527–34 (1903).—Goldschmidt welding process in use throughout the world. Also see 578–9, reporting a lecture by Goldschmidt. 19 pictures, 1 figure. *More popular than article (3): processes, products. Chemical. Engineering: equipment design. 1 hr. 40 min.*

5. Theory and practice of sherardizing. SANG. *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), **5,** 187–9 (1907).—See article (24). *Popular: processes, products, properties, simple explanations, research. 50 min.*

6. Thermite welding in American practice. *Electrochem. & Met. Industry* (now *Chem. & Met. Eng.*), **6,** 166–8 (1908).—Instructions for using thermite. 5 pictures, 2 figures. *Popular: processes, little chemistry. Instructions more specific than in articles (3) and (4). 30 min.*

***7. Presentation of Perkin medal to Dr. Charles Martin Hall.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **9,** 69–72 (1911).—MCKENNA: introduction. CHANDLER: presentation. HALL: inventions, financial problems, personal reminiscences. HEROULT: reminiscences. 1 portrait. *Popular: historical, raw materials, processes, economics. Chemical: research. 1 hr. 20 min.*

***8. A novel development in laboratory burners and furnaces.** FISHER. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **9,** 222–4 (1911).—Excellent picture showing the temperatures of Meker and Bunsen burner flames. Melting gold, silver, and copper without a blast-lamp in a Meker burning flame. 2 pictures. *Popular: properties. 20 min.*

9. (Possible uses for rare elements.) WHITNEY. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **9,** 316–7 (1911).—Calcium, thallium, tellurium, cobalt, silicon, boron, vanadium, cadmium, and titanium; future uses. *Popular: properties, no processes or products. 30 min.*

***10. Reminiscences of Robert Wilhelm Bunsen.** GOLDSCHMIDT. *Met. &*

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* Contribution from the Frick Chemical Laboratory of Princeton University.

† Subsequent parts will outline other industrial and non-technical journals; and a yearly bibliography will keep the list up to date.

‡ Volumes **1–7,** *Electrochemical and Metallurgical Industry;* Volumes **8–18,** *Metallurgical and Chemical Engineering;* Volumes **19–41,** *Chemical and Metallurgical Engineering.*

Chem. Eng. (now *Chem. & Met. Eng.*), **9**, 569–71 (1911).—Interesting anecdotes illustrating Bunsen's character and scientific zeal. *Popular: research. 50 min.*

*11. **Presentation of the Perkin medal to Herman Frasch.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **10**, 73–82 (1912).—CHANDLER: presentation, Frasch's life-history, deodorizing oil, other oil ventures, work on sulfur. FRASCH: reply, methods of desulfurization of oil, roasting-furnaces, problems involving California oils, oil fields of the coastal plains, sulfur, the Frasch sulfur process, geology, sulfur in U. S. and Sicily. Excellent résumé. 9 pictures. *Popular: historical, raw materials, processes, products, properties, economics. Chemical: research. Engineering: equipment design. 3 hrs.*

12. **Synthetic ammonia. An account of the report of Professor Haber which led the Badische Company to take up the process on a large scale.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **11**, 211–4 (1913).—Highly theoretical; Haber and Le Rossignol's experiments of historical interest. See also editorial on **The Haber synthetic ammonia process.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **11**, 173–4 (1913).—3 figures, 1 graph. *Chemical and Engineering only: processes, research, advanced, equipment design. Difficult, technical reading. Caution: remember different catalysis are used today. 1 hr. 20 min.*

13. **The manufacture of petroleum products.** ROBINSON. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **11**, 389–94 (1913).—Groups of petroleum products, physical and chemical properties of the crude oils, and properties of refined products from distillation and cracking. 2 flow sheets, 4 pictures of equipment, 3 graphs. *Popular: raw materials, processes, products, properties, no organic required. Chemical. Engineering: equipment design, technical. 1 hr. 40 min.*

14. **Presentation of the Perkin medal to John W. Hyatt.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **12**, 131–6 (1914).—Early history of celluloid, continuous water filtration, other industrial inventions of Hyatt. THOMPSON: biography. CHANDLER: presentation. HYATT: acceptance, invention of celluloid, anecdotes, personal reminiscences, and patents. 1 portrait. *Popular: historical, processes, products, no organic required, research. 2 hrs.*

*15. **The application of physical chemistry to industrial processes.** RITTMAN. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **12**, 475–8 (1914).—Principles of chemical equilibria applied to the fixation of nitrogen by the arc and Haber processes, contact sulfuric acid, oxides of carbon from the blast furnace, coefficient of partition of a solid between two liquids. *Chemical and Engineering only: research, advanced, mathematics. 1 hr. 10 min.*

16. **Some aspects of industrial chemistry.** BAEKELAND. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **12**, 557–66 (1914).—Beginnings of chemical industries in France, England, and Germany; stimulating influence of the dye industry on organic chemistry; industrial research laboratories, international scope of chemical research; nitrogen fixation for fertilizers; necessity of scientific teamwork and good financial backing; natural deposits of soda; LeBlanc soda, Solvay process, electrolytic process a new competitor; organic chlorine compounds, electrolytic alkali cells, cheap power not the only factor, gas power, new power centers to compete with water power, advanced methods of agriculture, future for chemistry, ignorance of natural resources, reason for America's slow development of chemical industries, imports and exports between U. S. and Germany, pioneer research and industries in America, efficiency versus waste, new scientific education and government by engineers or lawyer-politicians. *Popular: historical, raw materials, processes, properties, products, economics. Chemical. Engineering. 3 hrs. 20 min.*

17. **Chemistry and lighting.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **13**, 50–5 (1915).—Incandescent gas mantle, thoria treatment; history of arc carbons; and, briefly, quartz-mercury lamp and electrodeless discharge. Antedated processes. *Popular: historical, products, properties. Chemical. 1 hr. 50 min.*

*18. **The chemical industries of Germany.** FRANKLAND. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **13**, 378–87 (1915).—Porcelain, glass, cyanides, beet-sugar, sulfuric acid, soda and bleaching-powder, hydrogen, artificial illumination, ammonia, fixation of nitrogen by inorganic means, potash salts, explosives, artificial silk; synthetic organic chemistry including dyes, drugs, and perfumes; proposed coal-tar and other industries in Great Britain. *Popular: historical, processes, products, economics, no organic required, but helpful. Chemical. Engineering. 3 hrs.*

19. **Chemical principles of the blast furnace.** JOHNSON. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **13**, 536–43 (1915).—Theory of reactions involving oxides of iron, oxides of carbon; phase-equilibrium diagrams, solution of carbons, action of hydrogen, carburization of iron, removal of sulfur; reduction of silicon, phosphorus, and manganese; slag, titanium, and the formation of cyanides and calcium carbide. 1 figure, 1 graph. *Engineering: equations, research, advanced, highly technical. 3 hrs. 40 min.*

*20. **The rubber industry.** KING. Part I: *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **14**, 23–9 (1916).—History, types of rubber, tapping process, latex, coagulation, physical and chemical properties, structural formula; synthetic rubber from phenols, corn, turpentine, pyrogenic reactions, petroleum; vulcanization. 5 pictures. *Part popular: historical, raw materials, processes, properties, no organic required. Part chemical: equations, research, advanced. 2 hrs.* Part II: *ibid.*, 71–7. Washing crude rubber, drying, compounding, mixing, calendering, frictioning, making rubber cement, vulcanization, manufacture of tires and rubber articles, dipped goods and reclaimed rubber. 5 pictures of machinery, 4 figures. *Engineering: processes, products, no organic required, equipment design. 2 hrs.*
Part III: Reclaiming of rubber waste. *Ibid.*, 309–11. Too technical.

21. **The turpentine industry in the southern states.** HERTY. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **14**, 427–34 (1916).—6 pictures, 8 tables. *Popular: raw materials, processes, products, little chemistry, no organic required. 2 hrs. 20 min.*

22. **Coal-gas residuals and their application.** WAGNER. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **14**, 493–500 (1916).—Destructive distillation of coal yielding coke, retort graphite, tar, naphthalene, cyanogen, ammonia, coal-tar, and benzol products; dyes. 1 flow sheet. *Popular: products, economics, no organic required. Chemical. 2 hrs. 10 min.*

23. **Niagara Falls power and American industries.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **14**, 507–12 (1916).—EDMANDS: problem of diverting water for power. TONE: excellent review of electric furnace products. HOOKER: industries which will develop from the power. Omit as obsolete: IV The Nitrogen Industry. *Popular: products, economics. 2 hrs.*

24. **The sherardizing process.** STORBY. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **14**, 683–91 (1916).—Coating with zinc vapor on iron, copper, and gold; zinc-iron alloys which are formed; testing their weathering properties; theory of sherardizing, zinc-dust control; see article (5). *Chemical: historical, processes, properties, research. 2 hrs. 30 min.*

25. **The metallurgy of the rarer metals.** RICHARDS. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **15**, 26–31 (1916).—Beryllium, magnesium, calcium, strontium, barium, boron, chromium, titanium, molybdenum, zirconium, and cerium. *Popular: products, properties, economics. Chemical. 1 hr. 50 min.*

26. **An explanation of the flotation process.** TAGGART AND BEACH. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **15**, 518–23 (1916).—Surface tension, adsorption, viscosity; application to flotation processes: film, froth, agitation, pneumatic-froth, and the Potter-Delprat processes. 1 picture, 6 figures. *Chemical: research, advanced, mathematics. Engineering. 1 hr. 40 min.*

*27. **The production of salt in Szechuen province, western China.** RICHARDSON. Part I: *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **16**, 32–40 (1917).—Drilling 4000-foot wells, pumping brine, transporting, evaporating, gas wells; curious blend of prehistoric and modern China. 15 pictures, 3 figures, 2 flow sheets. *Popular processes. Engineering: equipment design. 1 hr. 40 min.*
Part II: *ibid.*, **17**, 225–6 (1917).—Drilling; raising and evaporation of brine. 3 pictures, 2 figures. *Popular: processes. Engineering: equipment design. 30 min.*
Part III: *ibid.*, **17**, 313–6 (1917).—9 pictures, 1 flow sheet. *Popular: processes. Engineering: equipment design. 50 min.*

28. **Presentation of Perkin medal to Ernst Twitchell.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **16**, 141–6 (1917).—CHANDLER: presentation, history of Twitchell process. TWITCHELL: acceptance, brief personal account of his discovery. LANGMUIR: the Twitchell process and the glycerin trade. ITTNER: the Twitchell process in the soap and candle industry. SCHMIDT: an appreciation. 1 portrait. *Popular: processes, advanced, organic required. 1 hr. 40 min.*

29. **Synthetic rubber.** KING. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **16**, 511–8 (1917).—Structure and formulas; attempts to produce synthetic rubber from cracking of cyclic and straight-chain hydrocarbons: turpentine, petroleum, fats; condensations of acetylene, acetaldehyde, alcohols; opening the benzene ring, coal-tar; fermentation with starch, and by the acetaldehyde route; dehydration of alcohols and ethers. See articles on Duprene. *Chemical: historical, processes, research, advanced, organic required. 2 hrs. 30 min.*

30. **Porcelain.** BLEININGER. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **16**, 589–94 (1917).—Compositions of American, hard-fire, soft, bone-china, Parian, refractory, and special porcelains; effect of firing, physical properties, and defects in porcelain. Numerous tables. 3 pictures, 2 graphs. *Popular: processes, products, properties. Chemical. Engineering. 1 hr. 40 min.*

31. **How do the warring nations obtain their nitrogen supply?** NAUCHKOFF. *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **17**, 525–36 (1917).—Chile saltpeter, with excellent maps; atmospheric nitrogen using the Birkeland-Eyde, cyanamide, Serpek, and, briefly, the Haber in conjunction with the Ostwald Process; the warring nations' division of nitrogen. Caution: arc process obsolete; cyanamide process displaced by Haber and Claude Processes. 10 pictures, 9 figures, 2 maps. *Popular: raw materials, processes, products, economics. Chemical. Engineering: equipment design. 3 hrs. 40 min.*

32. **Mineral resources of the Appalachian south.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **18**, 449–59 (1918).—Series of short articles listing mineral deposits in Alabama, Georgia, Maryland, North Carolina, Tennessee, Virginia, and West Virginia. 14 pictures, 1 map. *Chemical: raw materials, economics, excellent for a geologist. 3 hrs.*

33. **The California kelp operations of the Hercules Powder Company.** *Met. & Chem. Eng.* (now *Chem. & Met. Eng.*), **18**, 576–80 (1918).—Acetone recovery for use in munitions. 12 pictures. *Popular: processes. Chemical: organic required. Engineering: equipment design. 50 min.*

34. **Potash from Searles lake.** ROPP. *Chem. & Met. Eng.*, **19**, 425–31 (1918).—Salting, prospecting, evaporation, crystallization, raw materials, products, storing, and crystallizing machinery. 15 pictures, 3 maps. *Engineering: processes, little chemistry, equipment design. 1 hr. 20 min.*

35. **The rôle of colloids in chemical processes.** *Chem. & Met. Eng.*, **19**, 630–2 (1918).—A résumé of Jerome Alexander's "Colloid Chemistry." Colloid uses in ceramics, metallurgy, soap, milk, canning, rubber, photography, foods, and living organisms. *Popular: properties. Chemical. 1 hr.*

36. **Commercial uses of chlorine.** KOKATNUR. *Chem. & Met. Eng.*, **19**, 667–71 (1918).—Commercial uses of chlorine, exhaustive list of poisonous gases, inorganic chlorine compounds; and organic chlorine compounds such as coal-tar intermediates, medicinals, and solvents; names and formulas. *Chemical: products, properties, advanced, organic required. 1 hr. 40 min.*

*37. **Aluminium-manufacturing processes used in Europe.** NISSEN. *Chem. & Met. Eng.*, **19**, 804–15 (1918).—Descriptions of processes, cryolite baths, carbon electrodes, electric insulation, and industrial applications. Cross-sections of furnaces. 25 figures of machinery, 1 graph. *Engineering: historical, processes, equations, research, advanced, equipment design. 3 hr. 20 min.*

38. **The oxidation of ammonia.** LANDIS. *Chem. & Met. Eng.*, **20**, 470–7 (1919).—Early discoveries, the Ostwald process, the process used in England, types of apparatus, German developments during the war, demonstration plant in New Jersey, and life of the catalyst. 5 figures. *Chemical: historical, processes, advanced. Engineering: equipment design. 2 hrs. 20 min.*

39. **Uses of manganese dioxide ore.** PHALEN. *Chem. & Met. Eng.*, **21**, 196–9 (1919).—Manganese in the dry cell, glass industry, paint driers; miscellaneous manganese chemicals. *Chemical: products, equations, considerable chemistry. 1 hr. 20 min.*

40. **Natural industrial resources of the north central states.** *Chem. & Met. Eng.*, **21**, 308–41 (1919).—Chicago district, Indiana, Michigan, Wisconsin. 5 maps, 34 pictures. *Popular: raw materials, economics. Selections.*

*41. **The need for research in the non-metallic field.** LADOO. *Chem. & Met. Eng.*, **21**, 348–52 (1919).—Economic importance of non-metallic minerals, their value and adaptability to other industries, their influence on the daily life of the community, need for engineering research. 11 pictures. *Popular: raw materials, properties, economics, Chemical: research. Engineering. 1 hr. 10 min.*

*42. **Pure gum shellac.** JONES. *Chem. & Met. Eng.*, **21**, 715–21 (1919).—11 pictures. *Popular: historical, raw materials, processes, products, properties, no organic required, interestingly written. 2 hrs. 40 min.*

43. **The manufacture of pure tungsten metal.** JONES. *Chem. & Met. Eng.*, **22**, 9–16 (1920).—Operations of the Fansteel Products Company; treating the refined ore, roasting, design of furnace, leaching, commercial tungstic acid and its purification, tungstic oxide, tungsten powder, structural detail of the reduction furnace, properties of the metallic tungsten, and a brief résumé of uses of tungsten aside from in the steel industry. 14 pictures, 2 figures. *Popular: processes, products, properties. Chemical: equations, considerable chemistry. Engineering: equipment design. 1 hr. 30 min.*

44. **The catalyst for the oxidation of ammonia.** PERLEY. *Chem. & Met. Eng.*, **22**, 125–9 (1920).—Catalysts used by Ostwald, Kaiser, Frank and Caro, American Cyanamide, Partington in England, Bureau of Mines; theories of the surface reaction, the spacing of the gauzes, effect of voids between the catalyst layers, and the influence of the space-velocity, time, and temperature. Excellent résumé. *Popular: processes. Chemical: equations, research. Engineering. 1 hr. 40 min.*

45. **Some developed mineral resources and chemical industries of the southern states.** FAIRLIE. *Chem. & Met. Eng.*, **22**, 307–12 (1920).—Phosphate rock of Florida and Tennessee for commercial fertilizers; sulfur, pyrites, pyrrhotite, manufacture of sulfuric acid, and smelting of copper. 4 pictures, 1 graph. *Popular: raw materials, economics. Chemical. 1 hr. 50 min.*

*46. **Pictorial description of the cotton-oil industry.** WESSON. *Chem. & Met. Eng.*, **22**, 465–72 (1920).—Pictures of steps in cotton-oil industry from the picking of cotton to the final products. 54 pictures, 4 figures, 3 graphs. *Popular: processes, products, no organic required, little chemistry. Engineering. 1 hr. 30 min.*

47. **The sterilization of water by means of ultra-violet rays.** DECKER. *Chem. & Met. Eng.*, **22**, 639–45 (1920).—Microörganisms in water and their identification; sterilization with chlorine and with ultra-violet rays, rate of consumption of water. 4 figures, 6 graphs. *Popular: historical, processes, properties. Chemical: research. Engineering. 1 hr. 50 min.*

48. **Technical application of hydrogen in hydrogenation or hardening of oils.** BARNITZ. *Chem. & Met. Eng.*, **22**, 745–8 (1920).—Soap, edible oils, the hydrogenation process, preparing the catalyst, and source of hydrogen. 4 figures. *Popular: processes, properties, no organic required. Engineering: equipment design. 1 hr. 10 min.*

49. **A comparative test upon high-speed steels.** LANGHAMMER. *Chem. & Met. Eng.*, **22**, 829–32 (1920).—Part I: carbon steels, self-hardening, high-speed, stellite, soft and English steels; the effect of tungsten, vanadium, chromium, molybdenum, uranium, cobalt, manganese, and carbon on steels. [Parts II–IV later on in this volume are too technical.] *Excellent summary. Popular: properties. 1 hr. 20 min.*

50. **Manufacture of potassium permanganate.** STRINGFIELD. *Chem. & Met. Eng.*, **22**, 1027–30 (1920).—Process carried out in Southern California, and analytical methods used in controlling process. 3 figures. *Chemical: processes, equations, research, advanced. Engineering: equipment design. 1 hr.*

51. **Nitrogen fixation by the Haber method.** JONES. *Chem. & Met. Eng.*, **22**, 1071–5 (1920).—Theoretical considerations of preparation of gauzes and catalyst, plants in the U. S., comparison with the cyanamide process; excellent résumé up to 1920. 6 pictures. *Popular: processes, economics. Chemical: research. Engineering. 1 hr. 30 min.*

52. **Philippine industrial material, products and resources available to the United States.** COX. *Chem. & Met. Eng.*, **23**, 137–44(1920).—Alcohol, sugar, coconut shells, fibers, rubber, resins, leather, paper pulp, insect powders, and minerals. 2 pictures. *Popular: properties, economics. 1 hr. 30 min.*

53. **Putting the vegetable oil industry on a scientific basis.** BAILEY. *Chem. & Met. Eng.*, **23**, 441–6 (1920).—Problems in producing crude oils from stock; laboratory refining and manufactured products including driers, china-wood oil, polymerization, rubber substitutes, artificial leather, lard, butter-substances, and soap manufacture. 3 pictures. *Popular: processes, products, no organic required. Chemical: research. 1 hr. 50 min.*

*54. **Pure metallic arsenic.** JONES. *Chem. & Met. Eng.*, **23**, 957–60 (1920).—Production, properties, and uses of arsenic trioxide, and metallic arsenic. 7 pictures. *Popular: processes, products, properties. Chemical: equations, much chemistry. 30 min.*

55. **Notes on nickel.** MERICA. *Chem. & Met. Eng.*, **24**, 17–21 (1921).—Sources, metallurgy, uses, forging, welding, electrodeposition; source of nickel used in electroplating; nickel baths. 1 graph. *Popular: processes, products. Chemical. 1 hr. 20 min.*

*56. **Engineering problems in dust explosion prevention.** PRICE. *Chem. & Met. Eng.*, **24**, 29–32 (1921).—Explosion temperatures of gases; of dusts such as flour, sugar, cork, etc.; effect of humidity. 4 pictures of dust explosions. *Popular: properties. Chemical: research. 60 min.* **Preventing dust explosions.** *Ibid.*, 473–5.—Atmospheres of low oxygen content, inert dust, dust removal. 2 pictures, 2 figures. *Popular: properties. Chemical: research. Engineering. 40 min.* **An explosion of hard rubber dust.** (PRICE AND BROWN.) *Ibid.*, 737–40.—Theories of explosion, recommended precautions. 3 pictures, 2 figures. *Popular: properties. Chemical: research. Engineering. 50 min.*

57. **Recent advances in the American sulfur industry.** BACON AND DAVIS. *Chem. & Met. Eng.*, **24**, 65–72 (1921).—Sulfur versus pyrites for sulfur dioxide, effect of petroleum on combustion, sulfur for insulating material and water-proof cements, tabulation of the physico-chemical properties of sulfur, and a chart of the uses of sulfur. 22 pictures, 2 figures. *Popular: raw materials, processes, products, properties, economics. Chemical. Engineering. 1 hr. 40 min.*

*58. **Presentation of Perkin medal to Willis R. Whitney.** *Chem. & Met. Eng.*, **24**, 99–107 (1921).—LITTLE: biographical reminiscences. CHANDLER: presentation; the medalist's accomplishments, his publications. WHITNEY: acceptance, the biggest things in chemistry. *Popular: research, philosophical. 2 hrs. 50 min.*

59. **A comparison of various methods of water purification.** TAYLOR. *Chem. & Met. Eng.*, **24**, 123–9 (1921).—Distillation, filtration, Zeolite filters, precipitation water-softeners, water for use in laundries and textile mills, boiler compounds, advantages of the different types, preventing corrosion, and large installations. Excellent résumé. *Popular: processes, properties. Chemical: equations. Engineering. 2 hrs. 10 min.*

60. **Salt manufacture in Michigan.** BADGER. *Chem. & Met. Eng.*, **24**, 201–7 (1921).—10 pictures, 7 figures. *Engineering: processes, equipment design. 1 hr. 50 min.*

61. **Recovery of sugar from beet-molasses.** MONTGOMERY. *Chem. & Met. Eng.*, **24**, 605–8 (1921).—Precipitation of sugars by Steffans (lime) process, and strontia process. 2 pictures, 3 flow sheets. *Popular: processes. Chemical. Engineering. Good chemical description. 60 min.*

62. **The Alsatian potash industry.** VIGNERON. *Chem. & Met. Eng.*, **24**, 655–61 (1921).—Location of sylvinite (sylvite) deposits, mining methods, surface treatment, choosing and testing operating methods, and distribution of product. 11 pictures, 2 figures, 1 graph, 2 maps. *Popular: raw materials, processes, research. Engineering: equipment design. 1 hr. 40 min.*

63. **Salts refining plants at Owens and Searles lakes.** CHAPMAN. *Chem. & Met. Eng.*, **24**, 683–8 (1921).—Production of natural sodium carbonate, sodium borate, and potash; recovery processes, and different firms engaged in this recovery. 7 pictures, 2 maps. *Popular: raw materials, processes. Chemical. Engineering: equipment design. 1 hr. 30 min.*

64. **Award of the Nichols medal to Gilbert N. Lewis.** *Chem. & Met. Eng.*, **24**, 869–75 (1921).—LAMB: appreciation; introductory remarks about Lewis. JOHNSON: personal reminiscences. TEEPLE: presentation. LEWIS: **Color and chemical constitution.** Atomic structure in inorganic and in organic chemistry as being responsible for the colors of atoms and molecules; Lewis structure of the atom. Portrait. *Chemical: no organic required, research, advanced. 2 hrs. 20 min.*

65. **Oils, fats, and waxes in Latin-America.** WILSON. *Chem. & Met. Eng.*, **24**, 1101–8 (1921).—Seed-oils, vanilla and tonka beans; animal fats; waxes. 8 pictures. *Popular: raw materials, properties, no organic required. 2 hrs. 20 min.*

*66. **Presentation of the Gibbs medal to Mme. Curie.** *Chem. & Met. Eng.*, **24**, 1132–40 (1921).—Addresses on the application of radium in chemistry, physics, geology, astronomy, and medicine. Address by Mme. Curie, outlining her hunt for radioactive elements, separation of radium, rays from radium, transformation of radioactive elements, and their chemistry. *Popular: historical, processes, properties. Chemical: research. 2 hrs. 50 min.*

*67. **The dependence of the lime industry upon nature and science.** LITTLE. *Chem. & Met. Eng.*, **25**, 149–52 (1921).—Occurrence and origin of calcium carbonate in nature, limestone, chalk, nummulitic limestone, coral, pearls, marble; science and the lime industry; a general résumé. *Popular: raw materials, properties, cultural. Chemical: research. 1 hr. 10 min.*

*68. **The chemistry, manufacture and uses of nitrocellulose.** SCHLATTER. *Chem. & Met. Eng.*, **25**, 281–6 (1921).—Early history of nitrocellulose, relation to the chemistry of cellulose, use in war and peace, plastics, artificial silk, leather, medicine, and photography. 6 pictures. *Popular: historical, old and new processes, products, properties, no organic required. Chemical. 1 hr. 40 min.*

*69. **The manufacture of nitroglycerine.** SYMMES. *Chem. & Met. Eng.*, **25**, 831–4 (1921).—Like article (68). 4 pictures. *Popular: processes, properties, no organic required. Chemical: equations.*

70. **Manufacture of cellulose nitrate for pyroxylin plastics.** DU PONT. *Chem. & Met. Eng.*, **26**, 11–6 (1922).—Raw materials, methods of nitration, purification of cellulose nitrate, washing, pulping, bleaching, and drying. 3 pictures, 2 figures. *Engineering: processes, properties, no organic required, equipment design. 1 hr.*

71. **Manufacture of pyroxylin plastics.** DU PONT. *Chem. & Met. Eng.*, **26**, 65–70 (1922).—Properties of celluloid, mixing cellulose nitrate with camphor and alcohol, stabilizing, filtering, rolling, baking, sheeting, seasoning, polishing, manufacture of rods and tubes; search for substitutes. 6 pictures of machinery. *Engineering: processes, products, properties no organic required, equipment design. 1 hr.*

72. **Explosives and fertilizers.** WHITE. *Chem. & Met. Eng.*, **26**, 161–5 (1922).—Nitrogen preparedness—1914 and 1922; preparedness for peace, the chemical engineer's responsibility. *Popular: processes, properties, economics. Engineering. 1 hr. 20 min.*

*73. **The explosibility of ammonium nitrate.** MUNROE. *Chem. & Met. Eng.*, **26**, 535–42 (1922).—Chemical properties, uses of ammonium nitrate and nitrous oxide, explosives and fertilizer, history of ammonium nitrate, accidents involving ammonium nitrate, recent test with ammonium nitrate. *Popular: historical, properties. Chemical: equations, research. 2 hrs. 10 min.*

*74. **Atoms and isotopes.** HENDRICK. *Chem. & Met. Eng.*, **26**, 583–7 (1922).—Excellent résumé of isotopes. Caution: the short section on nuclear structure is obsolete. *Popular: historical. Chemical: research. 1 hr. 40 min.*

*75. **Minerals, earths, and clays of Latin-America.** WILSON. Part I: *Chem. & Met. Eng.*, **26**, 631–6 (1922).—Chile saltpeter, copper mining, gold and silver, tin in Bolivia; iron industry lacks coal. 14 pictures. *Popular: raw materials, economics. 1 hr. 40 min.*
Part II: *ibid.*, 697–700. Manganese from Brazil, chromium, tungsten, vanadium, molybdenum, and cobalt. 5 pictures. *Popular: raw materials, economics. 1 hr.*
Part III: *ibid.*, 745–9. Bauxite, platinum in Colombia; zinc and lead in Mexico; antimony, bismuth, and mercury in Bolivia; monazite sand; asphalt in Trinidad; graphite; sulfur, borax, phosphates, mica, potash, and precious stones. 6 pictures. *Popular: raw materials, economics. 1 hr. 30 min.*

76. **New aluminium alloys of high strength.** *Chem. & Met. Eng.*, **26**, 689–94 (1922).—Cast and wrought alloys, best treatment, permanence, age-hardening with magnesium and silicon, microphotographs, and composition of alloys. [See also JEFFRIES: *Chem. & Met. Eng.*, **26**, 750–4 (1922).] 5 figures. *Chemical: products, properties. Engineering. 1 hr. 50 min.*

77. **New developments in the American glass industry.** MONTGOMERY. *Chem. & Met. Eng.*, **26**, 788–93 (1922).—Glass-making machinery and furnaces. 9 pictures. *Popular: processes, products, little chemistry. Engineering: equipment design. 1 hr. 30 min.*

78. **Up-to-date methods in the bleaching-powder plant.** MONTGOMERY. *Chem. & Met. Eng.*, **26**, 1038–42 (1922).—6 pictures, 2 figures. *Engineering: research, equipment design. 1 hr. 30 min.*

79. **The manufacture of ammonium nitrate.** SYMMES. *Chem. & Met. Eng.*, **26**, 1069–74 (1922).—Impurities in the ammonia and nitric acid, operating the still, scrubbers, neutralizing tubes, evaporating equipment, and crystallizing kettles; a short résumé of the use of ammonium nitrate in explosives. 5 pictures. *Chemical: processes, equations, research, advanced. Engineering: equipment design. 1 hr. 40 min.*

80. **The technology of carbon electrode industry.** MANTELL. Part I: **The history of its development.** *Chem. & Met. Eng.*, **27**, 109–12 (1922).—Evolution of electrode industry, artificial graphite, electric furnace electrodes, and recent developments. *Popular: historical, processes, products. Chemical. Engineering. 1 hr. 10 min.* Part II: **Raw materials for the electrode manufacture.** *Ibid.*, 161–4.—Physical and chemical properties of carbonaceous substances viewed from the standpoint of electrode requirements: petroleum, coke, pitch, natural graphite, tars. *Popular: raw materials, properties. Chemical. Engineering. 1 hr. 30 min.*
Part III: Omit.

81. **The manufacture of printing inks.** ANSTEAD. *Chem. & Met. Eng.*, **27**, 304–8 (1922).—Printing inks, varnishes, driers, retarders in the oils; the pigments themselves, including organic color-lakes, bases for color lakes, other ink pigments; manufacturing, testing, requirements for, and the classes of, printing inks. 1 picture. *Popular: products, properties, knowledge of organic helps. Chemical. 1 hr. 40 min.*

*82. **War explosives in France.** CAVALIER. *Chem. & Met. Eng.*, **27**, 689–93 (1922).—Problem of substitutes for picric acid explosives, since French lacked raw materials; fundamental explosive properties including sensitiveness, velocity of detonation, density limit; the, ammonium nitrate and chlorate explosives. 1 figure. *Chemical: properties, equations, advanced, mathematics. 1 hr. 30 min.*

83. **Art and science of leather manufacture.** SEYMORE-JONES. Part I: *Chem. & Met. Eng.*, **27**, 1110–4 (1922).—Tanning, hides, flaying, salting, defects in hides, skin structure, and chemical nature of the skin. 4 pictures. *Popular: raw materials, processes, properties, no organic required. 1 hr. 30 min.*
Part II: *ibid.*, 1253–8.—Preliminary wet-work, wetting, loosening hair by enzymes, acids and liming, softening agents, and pickling, rounding, and splitting. 11 pictures of machinery. *Popular: processes, no organic required. Chemical. Engineering. Technical but interesting. 1 hr. 30 min.*
Part III: *ibid.*, **28**, 200–5.—Vegetable tanning, an entirely different process from parts I–II. 13 pictures. *Popular: raw materials, processes, products, no organic required. 1 hr. 20 min.*
Part IV: *ibid.*, **28**, 400–3.—Additional tanning methods, chrome liquors, iron tannage, formaldehyde, chamois, quinone-tannage, patent leather, fish-leather, water supply, and by-products. Summarizes by-products more than parts I–III. *Popular: processes, products, no organic required. 1 hr. 10 min.*

84. **A glimpse of the liquid carbon dioxide industry.** WIKOFF. *Chem. & Met. Eng.*, **28**, 5–9 (1923).—Manufacturing; compressing; and use. 9 pictures, 1 flow sheet. *Popular: processes, products, no organic required. Chemical. Engineering: equipment design. 1 hr.*

85. **Manufacture of spark-plug porcelain.** WIKOFF. *Chem. & Met. Eng.*, **28**, 150–7 (1923).—Research in testing and proving new materials. 23 pictures. *Popular: processes, research, little chemistry; for non-chemists. Engineering: equipment design. 1 hr. 50 min.*

*86. **Synthetic ammonia by the Claude process.** *Chem. & Met. Eng.*, **28**, 498–501 (1923).—Advantages of the Claude over the Haber-Bosch process. 5 pictures, 3 figures, 1 graph. *Chemical: processes, research, advanced. Engineering: equipment design. Clearly presented. 1 hr.*

*87. **Some research of general interest in progress at the Mellon Institute.** WIKOFF. *Chem. & Met. Eng.*, **28**, 625–32 (1923).—Researches on vitaminous bread, carbon dioxide, coke, corrosion, fiber containers, gelatin, insecticides, insulation, laundering, magnesium products, galvanizing, mundacizing cleaning, nickel and monel metal, refractories, vitrified tile, and wood chemicals. 5 pictures, 4 portraits. *Popular: products, properties. Chemical: research. Engineering. 2 hrs.*

88. **Manufacture of activated carbon.** RAY. *Chem. & Met. Eng.*, **28**, 977–82 (1923).—Structure; detailed problems in carbon manufactured by the Chaney process, and variations in the properties of the products obtained. See also: **Abatement of industrial stenches by means of activated carbon.** RAY AND CHANEY: *ibid.*, **28**, 1114–6 (1923). 2 graphs. *Popular: processes, properties, no organic required. Chemical: research. 1 hr. 50 min.*

89. **Chemical engineering in the production of coated fabrics.** KIRKPATRICK. *Chem. & Met. Eng.*, **28**, 1017–23 (1923).—Manufacture of artificial leather and rubberized cloth. 15 pictures, 2 figures. *Engineering: processes, no organic required, equipment design, little chemistry. 1 hr. 50 min.*

90. **The production of book paper.** PAYNE. Part I: *Chem. & Met. Eng.*, **29**, 831–7 (1923).—Preparation of wood, making sulfite acid, digesting and refining the pulp. 11 pictures, 2 figures. *Popular: raw materials, processes, no organic required. Engineering: equipment design. 1 hr. 40 min.*
Part II: *ibid.*, 959–62.—Thick bleaching sulfite pulp. 6 pictures, 1 figure. *Engineering: processes, no organic required, equipment design, technical. 1 hr. 10 min.*
Part III: *ibid.*, 1176–80.—De-inking, washing, and refining, treatment of paper, and the water system. 10 pictures. *Popular: processes, no organic required. Engineering: equipment design. 1 hr. 20 min.*

91. **The industrial utility of cobalt.** MASON. *Chem. & Met. Eng.*, **29**, 1135–7 (1923).—Chemical reactions and physical properties of cobalt; electroplating; cobalt steels, including stellite; and cobalt non-ferrous alloys. 2 pictures. *Popular: processes, products, properties. Chemical: research. 50 min.*

92. **Clear fused quartz.** BERRY. *Chem. & Met. Eng.*, **30**, 715–7 (1924).—3 pictures. *Popular: products, properties, little chemistry. 40 min.*

*93. **Production and use of refined sulfur.** NEWHALL. *Chem. & Met. Eng.*, **31**, 144–9 (1924).—Refining, forms of commercial sulfur in fertilizers, insecticides, preservation of food; uses of flowers of sulfur. 8 pictures, 2 figures. *Popular: processes, products, properties. Chemical. Engineering: equipment design. 1 hr. 50 min.*

*94. **The new pyroxylin automobile finish.** KIRKPATRICK. *Chem. & Met. Eng.*, **31**, 178–82 (1924).—How the Du Pont Company developed Duco; nitrating process, dehydrating with alcohol, dissolving in gums and pigments. 11 pictures. *Popular: processes, products. Chemical: research. Engineering: equipment design. 1 hr. 20 min.*

95. **Manufacture of refined cane sugar.** ALLEN. *Chem. & Met. Eng.*, **32**, 350–60 (1925).—Details for obtaining different types of sugar. 23 pictures, 4 flow sheets. *Popular: processes, products, no organic required, little chemistry. Engineering: equipment design. 2 hrs.*

*96. **Sulfur and industrial necessity.** LINT. *Chem. & Met. Eng.*, **32**, 365–9 (1925).—Production, and considerable economic discussion on the uses of sulfur and its compounds. 6 pictures, 2 figures, 7 graphs. *Popular: products, economics. Chemical. Engineering. 1 hr. 30 min.*

*97. **A pageant of progress.** *Chem. & Met. Eng.*, **32**, 729–44 (1925).—Interesting pictures comparing ancient and modern industrial processes for: thickening, making acids, leather, paint, paper pulp, soap, crushing, ceramics, glass, sugar, drying, cement, coke, petroleum, and evaporation processes. Short legend under each picture, otherwise no written material. *Popular only: processes, equipment design. 1 hr. 30 min.*

98. **Manufacture of rayon—chemical textiles.** KIRKPATRICK. *Chem. & Met. Eng.*, **32**, 844–7 (1925).—Operations at the Du Pont Rayon Company by the Viscose method, which is described in detail. 11 pictures. *Popular: processes. 50 min.*

99. **Producing clear fused quartz electrothermically.** BERRY. *Chem. & Met. Eng.*, **32**, 915–6 (1925).—Quartz ware, comparison between glass and quartz thermometers, gallium-in-quartz thermometer. See article (92). 1 picture. Considerable data but short. *Popular: historical, processes, properties. 40 min.*

100. **How sulfur is mined with superheated water.** LUNDY. *Chem. & Met. Eng.*, **32**, 917–9 (1925).—Frasch process and type of soil. 7 pictures. *Popular: processes. Engineering: equipment design. 30 min.*

101. **Increased demand features market for lead compounds.** HARN. *Chem. & Met. Eng.*, **33**, 37–40 (1926).—Industrial use of white lead, litharge, red lead, orange minerals, basic lead sulfate, blue basic lead sulfate, and sugar of lead; encyclopedia of commercial applications of oxides of lead. 1 portrait. *Chemical: products, properties, economics, research. 1 hr. 20 min.*

102. **Selling nitric acid to many industries.** RAND. *Chem. & Met. Eng.*, **33**, 487–8 (1926).—History of nitric acid industry, special precautions for shipping nitric acid, its properties, by-products, and industrial applications. *Popular: historical, processes, products, economics. Chemical. 40 min.*

103. **A basis for the future development of the chemical industry.** *Chem. & Met. Eng.*, **34**, 1–8 (1927).—Maps of the U. S. indicating production and consumption of chemicals, distribution of minerals and non-mineral raw materials; prices of chemicals, oils and fats; distribution of sulfuric acid, soda ash, caustic soda, nitrogen; imports and exports of materials. Entirely charts, no written matter. 4 maps, 8 figures, 3 graphs. *Popular: raw materials, economics. 1 hr. 20 min.*

104. **(Regional surveys of chemical possibilities in the United States.)** *Chem. & Met. Eng.*, **34**, 9–38 (1927).—Résumé of raw materials in Michigan, Dakota, California, Illinois, Indiana, Tennessee Valley, Kansas City district, Iowa, Rocky mountain district, Pacific Northwest, and St. Louis district. 101–8, Minnesota, Northern Ohio; 168–70, Montana, Idaho, Nevada, Utah; 299–305, Southern Ohio, New York; 364–71, New England, Georgia; 426–33, Western Pennsylvania, Oklahoma; 493–9, Alabama, Western Pennsylvania; 622–7, Texas, Florida; 686–91, Louisiana, Arkansas, Carolinas; and 750–7, Middle Atlantic States, Virginia, West Virginia, and Mississippi. *Popular: raw materials. Chemical. Selections.*

105. **Modern technology in producing pig aluminium.** MCBRIDE. *Chem. & Met. Eng.*, **34**, 76–82 (1927).—Theory of aluminium making, handling of cryolite, source of alumina, construction of pots and electrodes, making the aluminium, tapping the furnaces, and the capacity and future at Arvida, Canada. 8 pictures, 2 figures, 1 flow sheet. *Engineering: raw materials, processes, some chemistry, equipment design. 2 hrs.*

106. **Twenty-five years of American industry.** *Chem. & Met. Eng.*, **34**, 201–63 (1927).—Summary of the different industries including electrochemistry, engineering, rubber, glass, soap, petroleum, cane sugar, coal, dyes, explosives, paint, and paper. Many portraits. *Chemical: historical, processes, products, economics. Engineering. Selections.*

107. **Chemical engineering contributes to better lighting.** PIPKIN. *Chem. & Met. Eng.*, **34**, 660–3 (1927).—Frosting the inside of a lamp-bulb with hydrogen fluoride. See article (115). 5 pictures, 1 figure. *Popular: processes. Engineering: equipment design. 1 hr.*

108. **Anhydrous alcohol in America.** COOLEY. *Chem. & Met. Eng.*, **34**, 725–8 (1927).—Application of the principle of azeotropic mixtures in dehydrating alcohol to give absolute alcohol. 1 picture, 2 figures. *Chemical: historical, research, advanced, organic helps, patents, specialized. Engineering. 1 hr. 10 min.*

*109. **Interdependence through chemical engineering.** *Chem. & Met. Eng.*, **35**, 1–8 (1928).—Charts showing the inter-relation of individual industries: German Chemical combine, Allied Chemical and Dye, Du Pont, Union Carbide & Carbon Corporation, The Imperial Chemical Industries, and Les Établissements Kuhlmann. *Popular: products, economics. Engineering. 1 hr.*

110. **Chemical engineering in processes.** *Chem. & Met. Eng.*, **35**, 9–40 (1928).—In petroleum, paper, plastic, ceramic, coal, paint, fertilizer, vegetable oil, wood-distillation, rubber, foods, and textile industries. Engineering problems are reviewed, and the types of processes in each industry popularly summarized. 105–6, soap; 172–3, fine chemicals; 234–5, explosives; 361–3, heavy chemicals; and 751–3, cement. *Popular: raw materials, processes, products, properties. Chemical: research. Engineering. Selections.*

111. **Editorial impressions of economic and technical progress in German chemical industry.** PARMELEE. *Chem. & Met. Eng.*, **35**, 334–7 (1928).—9 pictures. Excellent but brief. *Popular: processes, products, economics. Chemical. Engineering. 1 hr.*

*112. **Map.** *Chem. & Met. Eng.*, **36**, front (1929).—Large colored map of world, showing distribution of raw and manufactured materials. No legend. 1 map. *Popular: raw materials, products, economics.*

*113. **Highly developed technique required to purify gases for "Neon" signs.** O'NEIL. *Chem. & Met. Eng.*, **36**, 143–4 (1929).—See article (116). 2 pictures. *Popular: processes, properties. 30 min.*

114. **Process control.** *Chem. & Met. Eng.*, **36**, 193–257 (1929).—Control of quality, prevention of accidents; automatic plant equipment in rubber, beet-sugar, cement, paper, natural gasoline, coal-products electrical control, gas analysis, caustic soda; and industrial instruments for control of temperature, pressure, and flow of liquids and gases. Many excellent illustrations. *Engineering: equipment design. Selections.*

115. **Chemical Engineering's contribution to the incandescent lamp.** *Chem. & Met. Eng.*, **36**, 408–9 (1929).—6 portraits. *Popular: historical, products, research. 30 min.*

116. **Coloring incandescent lamps on the inner surface.** LINDSTROM. *Chem. & Met. Eng.*, **36**, 410–1 (1929). See article (114). 1 picture. *Popular: processes, products, research. 30 min.*

*117. **High explosives.** LAMOTTE. *Chem. & Met. Eng.*, **36**, 460 (1929).—Types, chemical composition, and manufacture. 5 pictures. *Popular: historical, processes, properties, no equipment design. 1 hr.*

118. **X-raying the structure of industry.** *Chem. & Met. Eng.*, **37**, 1–8 (1930).—5 charts and a map showing the basic structure of the process industries, 2 maps of U. S. showing where heavy chemicals are made and consumed, a map of the world showing where nitrogen is produced and consumed, long-time trends in the chemical producing and consuming industries. Little written material. Selections from pages 9–64: Industrial progress in 1930. *Popular only: economics. 1 hr.*

*119. **Chemical warfare service saves millions for industry.** SADTLER. *Chem. & Met. Eng.*, **37**, 88–90 (1930).—Peace-time activities of the U. S. chemical warfare service: anti-fouling paints for barnacles, creosote for woodborers, fumigation gases, boll-weevil poisons, tear gases, carbon monoxide and poison gas peace-time protectors, and gas masks. 4 pictures. *Popular: products, properties, research. 50 min.*

120. **Pressure and temperature applied to industrial progress.** *Chem. & Met. Eng.*, **37**, 529–61 (1930).—A series of papers. Recommended: 544–52, high pressure in nitrogen fixation, maps showing distribution of high pressure industries in U. S., methanol, helium; 558–61, hydrogenation of oils. Profusely illustrated. *Engineering: equipment design. Selections.*

121. **Nitric acid produced from ammonia by modified pressure system.** FAUSER. *Chem. & Met. Eng.*, **37**, 604–8 (1930).—Theory and manufacturing details. 3 pictures, 2 figures, 2 graphs. *Chemical processes, equations, research, advanced, mathematics. Engineering. 1 hr. 30 min.*

122. **Sodium metasilicate: its place amongst industrial alkalies.** VAIL. *Chem. & Met. Eng.*, **37**, 736–40 (1930).—Composition of industrial product, pH of its solutions; tests on its cleansing properties compared with borax, caustic soda, tri-sodium phosphate, etc. 4 pictures illustrating tests, 1 figure, 3 graphs. *Strictly chemical: properties, research. 1 hr. 30 min.*

123. **Hydrogenation adapted to the oil refinery.** BOYER. *Chem. & Met. Eng.*, **37**, 741–5 (1930).—Major problems including conversion of refinery residues, improvement of low-quality lubricating stock, conversion of inferior-burning oil, finishing of naphthas, and production of anti-knock gasoline. 6 pictures. *Engineering: processes, products, properties, research. 1 hr. 30 min.*

124. **Liquid CO_2—how technology has harnessed the available sources.** REICH. *Chem. & Met. Eng.*, **38**, 136–41 (1931).—Obtaining carbon dioxide by absorption, fermentation; and purification by the Backhaus, silica gel, or Reich processes; natural springs and magnesite; compressing and liquefaction. 1 flow sheet, 2 pictures, 5 figures. *Not popular. Chemical: processes. Engineering: equipment design. 1 hr. 50 min.*

125. **The whys and hows of leather manufacture.** LEWIS AND LORD.

Part I: *Chem. & Met. Eng.*, **38**, 452–5 (1930).—Treatment of heavy hides. 2 pictures. *Popular: raw materials, processes, properties, no organic required. 1 hr. 10 min.*
Part II: **More whys and hows of leather manufacture.** *ibid.*, 592–4.—Manufacturing processes with light leather, uses of finished products. 5 pictures. *Popular: processes, products, properties, no organic required. 50 min.*

126. **Chemical costs.** *Chem. & Met. Eng.*, **39**, 1–8 (1932).—The production and distribution costs of typical chemicals, as compared with other commodities; chemicals and other materials consumed in process industries, sale channels for ten billion dollars' worth of goods, annually, by process industries. Charts only, with short legends. *Popular only: economics. 1 hr. 30 min.*

127. **Guarding against corrosion in acetic acid equipment.** OTHMER. *Chem. & Met. Eng.*, **39**, 136–9 (1932).—Materials for handling acetic acid, including rubber, wood, copper, silver, copper-alloys, duriron, stainless alloys, lead, bonded metals, tantalum, and aluminum. 6 pictures. *Popular: properties. Engineering: equipment design. 1 hr. 10 min.*

*128. **Laminated glass production brings technical refinement.** *Chem. & Met. Eng.*, **39**, 266–7 (1932).—Pittsburgh Plate Glass, "Duplate Corporation" processes. See also article (129). 3 pictures. *Popular: processes, products, properties. 30 min.*

*129. **Sightseeing at Corning.** *Chem. & Met. Eng.*, **39**, 310–3 (1932).—Blowing glass, Corning Glass Works, Pyrex. 8 pictures. *Popular: historical, processes. Engineering: equipment design. 1 hr. 10 min.*

130. **Vast raw material resources await chemical development.** WEIGEL. *Chem. & Met. Eng.*, **39**, 366–71 (1932).—Two maps of the U. S. showing oil, gas, salt and sulfur domes; petroleum, natural gas, coal and lignite, limestone, bauxite, and miscellaneous minerals in Arkansas, Louisiana, Oklahoma, and Texas. 3 pictures, 2 maps, 1 portrait. *Popular: raw materials, economics. 1 hr. 10 min.*

*131. **Carbon dioxide in industry.** JONES. *Chem. & Met. Eng.*, **40**, 76–9 (1933).—Sequel to article (84). In food refrigeration, hardening alloy steels, trimming golf-balls, as an explosive, rain-maker.
Many other actual and proposed uses. 1 flow sheet. *Popular: properties. Chemical. 1 hr.*

*132. **March of electrochemistry.** MANTELL. *Chem. & Met. Eng.*, **40**, 120–1 (1933).—A pictorial chart, with historical legend covering 1800–1932. 1 picture. *Popular: historical. Chemical. Engineering. 1 hr.*

133. **Looking back at fifty years in ammonia-soda alkali industry.** TRUMP. *Chem. & Met. Eng.*, **40**, 126–9 (1933).—Soda ash in America from 1880 onward, by-product coke development, technology underlying business success, international coöperation, and pioneering human relations. 1 portrait, 1 figure, 1 graph. *Popular only: historical, economics. 1 hr. 20 min.*

*134. **Chemical engineering marches on!** *Chem. & Met. Eng.*, **40**, 230–5 (1933).—Excellent résumé of finished products from the war up until 1932, including plastics, fertilizer, phosphorus, sulfuric acid, heavy chemicals, bromine and iodine, ceramics, and natural synthetic rubber. 5 pictures. *Popular: products, economics. Chemical: research. Engineering. 2 hrs.*

135. **Mining sulfur under water in Louisiana.** O'DONNELL. *Chem. & Met. Eng.*, **40**, 454–8 (1933).—Location of deposit, building plant, water heating, pumps, compressors, mining, production capacity, and future problems. 9 pictures, 3 figures. *Engineering: processes, economics, equipment design. 1 hr. 10 min.*

136. **What and where are the process industries of the South?** *Chem. & Met. Eng.*, **41**, 400–33 (1934).—Ethyl bromine plant, Southern Kraft, Freeport sulfur, Solvay, Matheson Alkali and Southern Alkali; fertilizers, sulfuric acid, mineral products, chemicals, explosives, petroleum, forest products, glass, ceramics, newsprint, soap, and glycerin. 33 pictures, 18 maps. *Popular: raw materials, processes, economics. Engineering. Selections.*

137. **Domestic iodine industry demands recognition.** MANNING. *Chem. & Met. Eng.*, **41**, 568–70 (1934).—Iodine from oil in California. 8 pictures. *Popular: processes, economics. Chemical. Engineering. 30 min.*

138. **Silver may be the answer to your corrosion problem.** ROGERS. *Chem. & Met. Eng.*, **41**, 631–3 (1934).—Silver lined equipment. 3 pictures. *Popular: processes, properties. Engineering: equipment design. 50 min.*

SUBJECT INDEX

Starred (*) articles are recommended. Articles in parentheses ( ) furnish incidental information only.

INORGANIC CHEMISTRY

(Arranged according to the Periodic Table)

Group 0 **Inert gases,**— *113. **He,**— *2, (120).
" Ia **H,**— 48, (*2, *18, 19, 123). **Alkali metals,**— 60, (130). **Na,**— *27, 133, (*1, 16, *18, 31, 63, 114, 122, 136). **K,**— 34, (*18, 50, 62, 63, *75).
" Ib **Cu, Ag, Au,**— (*75). **Cu,**— (45, *119, 127). **Ag,**— 138, (127).
" IIa **Alkaline earths,**— (30). **Be,**— (25). **Mg,**— (25, *75, 76, 87, 124). **Ca,**— *67, *87, (9, 25, 61, 110, 130). **Sr,**— (25, 61). **Ba,**— (25). **Ra,**— *66.
" IIb **Zn,**— 5, 24, (*75, *87). **Cd,**— (9). **Hg,**— (17, *75).
" IIIb **B,**— (9, 25, 63, *75, 122). **Al,**— 3, 4, 6, *7, *37, 76, 105, (*37, *75, 127, 130). **Ga,**— (99).
" IVa **Ti,**— (9, 25). **Zr,**— (25). **Ce,**— (25, *75). **Th,**— (9, 17).
" IVb **C,**— see organic chemistry.
Si,— 122, (9, 59, *75, 76). **Glass,**— 77, *113, 115, 116, *128, *129, (*18, 39, 106, 136). **Quartz,**— 92, (17). **Porcelain,**— 30, 85, (*18, 35, *87, *134, 136). **Sn,**— (*75). **Pb,**— *87, 101, (*75, 127).
" Va **V,**— (9, *75). **Ta,**— (127).
" Vb **NH_3,**— 12, 31, 51, *86, 133, *134, (*15, 16, *18, 22, 120). **HNO_3,**— 38, 44, 102, 121. **Nitrate explosives,**— *68, *69, 72, 73, 79, *82, 131, (*18, 106, 110, 136), see cellulose esters. **P,**— (45, 122, *134). **As,**— *54. **Sb,**— (*75). **Bi,**— (*75).
" VIa **Cr,**— (25, 49, *75). **Mo,**— (25, 49, *75). **W,**— 43, (49, *75). **U,**— (49).
" VIb **S,**— *11, 57, *93, *96, 100, 135, (45, *75, 130, 136). **Sulfuric acid,**— (*15, *18, 45, 97, 103, *134, 136). **Te,**— (9).
" VIIa **Mn,**— 50, (39, 49, *75).
" VIIb **Halogens,**— *27, 60, (63, 130, *134). **F,**— 107. **Cl,**— 34, 36, (16, 47, 62). **Br,**— (136). **I,**— (137). **Oxyhalogens,**— 78, (*18, 36, *82).
" VIII **Fe,**— 19, 49. **Ni,**— 55, (*87). **Co,**— 91, (49, *75). **Special steels,**— 43, 49, (9, 76, 91, 127, 131). **Pt,**— (*75).

ORGANIC CHEMISTRY

Carbon, oxides and carbonates. C,— *1, 80, 88, (17, 19, 22, 49, *75, *87, 97, 106, 110, 115). **CO_2,**— 84, 124, *131, (*15, 19, *87, *119, 136). Carbonates,— *67, 133, (16, 63).
Cellulose products. Cotton, (*46). Celluloid,— 14, 71. Cellulose esters, — *68, 70, 71, 89, *94, 98. Cotton,— (*46). Paper,— 90, 98, (52, 97, 106, 110, 114, 136). Silk,— (*18).
Dyes, (16, *18, 22, 64, 106).
Drugs, perfumes,— (*18, 36, *68).
Fats, waxes, soaps and oils,— 28, *46, 48, 53, 65, 120, (*11, 35, 97, 103, 106, 110, 136).
Fuels,— 13, 22, 123, (*11, 97, 106, 114, 130, 136).
General organic. Acetone,— 33. Alcohol,— 108, (52, 120). Chlorine compounds,— (16). Coal tars, —22, (36, 80, 106, 114). Flame,— *8. Non-metallic elements,— *41. Paints,— (39, 97, 106, 110). Printing inks,— 81. Shellac,— *42. Sugar,— 61, 95, (*48, 106, 114). War,— *119. Turpentine, 21.
Textiles. Fabrics,— *68, 98, (*87, 89, 110). Leather,— 83, 89, 125, (52, 53, *68, 97).
Rubber,— *20, 29, (35, 52, 53, 89, 106, 110, 114, 127, 134).

MISCELLANEOUS

Biographical. *1, 7, (*10, *11, 14, *58, 64, *66).
Branches of chemistry. Biochemistry,— (35, 36, 47, 59, *66, *67, *87, *119). Colloids,— 35. Electrochemistry,— *1, 23, 80, *132, (16, 39, 55, 106). Metallurgy,— 9, 25, 26, (35). Photochemistry,— 17, 64, 115, 116, (35, 47, *68). Physical chemistry,— *15. Thermochemistry,— *2, *8, see aluminum.
General inorganic. Color,— 65. Dust explosions,— *56, (35). Isotopes, — *74. Power (see fuels),— 23, (16). Research,— *58, (16). Water purification,— 47, 59, (14).
Natural resources. United States,— 32, 40, 45, 52, 104, 130. Other countries,— 65, *75.

THE ELIZABETH CLAY HOWALD SCHOLARSHIP

This scholarship was endowed by the late Ferdinand Howald, an alumnus of The Ohio State University, in memory of his mother, Elizabeth Clay Howald. Appointments will be made annually and the scholar will receive an honorarium of $3000 paid in 12 equal monthly installments.

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Prospective candidates may secure application blanks by addressing the Dean of the Graduate School, The Ohio State University. Applications must be filed with the Dean of the Graduate School not later than March 1st. The appointment will be made on April 1st and the term of appointment will begin July 1st.

SOME TESTS *for* METAL IONS MAKING USE *of* ORGANIC DYES*

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THE IDEA of testing for metallic ions by means of organic dyes and other organic compounds is by no means a new one. A number of current qualitative analysis texts make use of a few such tests. Aluminon (aurin tricarboxylic acid) seems to be considered a quite satisfactory test for aluminum.[1] Dimethylglyoxime of course has a wide use in testing for nickel. Likewise the Titan yellow test,[2] the Clayton yellow test,[3] and the *p*-nitrobenzeneazoresorcinol test, known as the "S. & O." test,[4] are all being used considerably to detect or confirm magnesium. Also, there is quite a long list of similar tests that have been observed but which do not seem to have come into any general use. These include: an alizarin test for aluminum; an ammonium dithiocarbamate test for silver; a dinitroresorcinol test for cobalt; an ethylene diamine test for cadmium; a cinchonine test for bismuth; and an anthranilic acid test for copper.

It was with the thought of extending the list somewhat and in the hope of finding some new and distinctive tests for metals where needed, that this short and by no means exhaustive study was made at Greenville College as an honors project by a senior major student in chemistry.

In general, the procedure was simple and consisted in adding a few drops of the dye solution to a 5-ml. portion of solution of the metal salt, then precipitating the metal as the hydroxide, carbonate, or sulfate. For the hydroxides either sodium hydroxide or ammonium hydroxide was used, depending somewhat on how amphoteric the metallic hydroxides might be. In precipitating the carbonates a 4 *N* solution of sodium carbonate was usually employed. However, in some cases a *N*/10 solution of sodium bicarbonate was used. For the sulfates any dilute solution of sulfuric acid was found satisfactory. When the dyes were sufficiently soluble in water, aqueous solutions were used. Otherwise, in most cases, a saturated solution of the dye in 50% aqueous methyl alcohol was used.

A relatively small number of dyes was used in these tests—only those which happened to be readily available; *i. e.*, aluminon, amaranth, malachite green, aniline yellow, Congo red, Clayton yellow, fluorescein, indigo carmine, methylene blue, methyl orange, methyl violet, naphthol yellow S, light green S.F., orange I, Ponceau 3R, rosaniline, erythrosine, and picric acid. The metal ions used were such as could be precipitated as either hydroxides, carbonates, or sulfates; *i. e.*, silver, lead, mercurous, mercuric, cadmium, bismuth, stannous, stannic, antimony, aluminum, zinc, copper, ferrous, ferric, manganese, calcium, barium, strontium, and magnesium.

Out of the three hundred or so possible combinations using one dye and one cation at a time, there were three rather distinctive color effects obtained which were not found to have been observed and recorded. These are as follows: a fluorescein test for lead, a fluorescein test for silver, and a napthol yellow S test for stannous tin. A more detailed description of each follows.

FLUORESCEIN TEST FOR LEAD

To 5 ml. of solution containing lead ions are added two drops of the saturated fluorescein solution in aqueous methyl alcohol. Ammonium hydroxide or sodium hydroxide is then added dropwise until precipitation occurs. A pink coloration usually appears at once. The pale pink- or rose-colored precipitate soon settles out. If no interfering ions are present the supernatant liquid usually retains the bright yellow color of the fluorescein in alkaline solution. This test is sensitive to the extent of one part of lead nitrate to five hundred parts of water in absence of other ions. The test is quite satisfactory even in presence of other cations, provided they are not present too greatly in excess of the lead. For instance, some colored ions such as ferric or copper in appreciable quantities obscure the pink color. However, when present in very small quantities the color may be observed. When mercurous ion is present it, of course, turns dark, obscuring the pink. But if the mercurous solution is very dilute the color may be observed before darkening occurs.

In all cases the pink color seems to be adsorbed by the lead hydroxide, although in some cases it may become obscured. In the presence of aluminum, magnesium, and antimony the pink color appears immediately on the addition of the reagent; but on standing it tends to be obscured by the other precipitates. It is rather striking that even in the presence of some colored ions such as cobalt and nickel the pink lead hydroxide settles

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* Presented before the Illinois Academy of Science, Bloomington, Ill., May 3, 1935.

[1] YOE AND HILL, *J. Am. Chem. Soc.*, **49**, 2395 (1927).

[2] KOLTHOFF, *Biochem. Z.*, **185**, 344 (1927); *Chem. Abstr.*, **21**, 2632 (1927).

[3] BARNES, *J. S. African Chem. Inst.*, **11**, 67 (1928); *Chem. Abstr.*, **23**, 1838 (1929).

[4] RUIGH, *J. Am. Chem. Soc.*, **51**, 1456 (1929).

out when an excess of ammonium hydroxide is added. This is especially true in the case of cobalt.

FLUORESCEIN TEST FOR SILVER

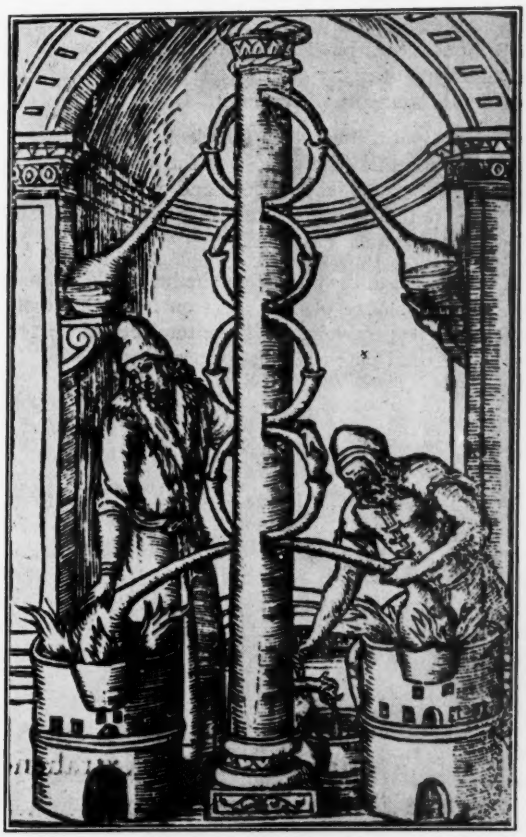
The only insoluble carbonate that seemed to adsorb any of these dyes to give a distinctive test is that of silver which also adsorbs fluorescein. The test is performed as follows:

To 5 ml. of a dilute silver salt solution one or two drops of a saturated solution of fluorescein in a water-alcohol mixture are added, and then 4 *N* sodium carbonate solution is added drop by drop. Much care must be used in order not to add too much reagent, as an excess will destroy the color. A pink- or rose-colored precipitate settles out. The question naturally arises here whether the precipitate adsorbing the color is silver carbonate or silver hydroxide. One would naturally presume that both silver carbonate and silver hydroxide would be precipitated under these conditions. However, to attempt to precipitate silver hydroxide by the addition of an ordinary solution of sodium hydroxide or ammonium hydroxide always produces a black silver oxide very shortly. It was learned, though, that on the addition of calcium hydroxide to the silver solution containing fluorescein there seemed to be formed a colloidal suspension of silver hydroxide which had adsorbed the dye in the usual manner, imparting the pink color to the entire solution. Also, when a *N*/10 ammonium hydroxide solution is used a similar appearance results. In time these two gradually darken and settle out, evidently as silver oxide. This test will detect silver when it is present in one part to five hundred parts of water. This test is satisfactory even in the presence of some other metal ions singly. However, the colorless ions—mercurous, mercuric, stannous, stannic, ferrous, and some of the colored ions, such as ferric and nickel, do interfere with this test. In the main the interference is evidently due to the interfering ion reducing the silver to black, finely divided metallic silver. Ammonium ions in all concentrations, and alkali metals in high concentrations, seem to interfere with this test.

A NAPHTHOL YELLOW S TEST FOR STANNOUS TIN

When two or three drops of a 2% solution of naphthol yellow S are added to a stannous salt solution and sodium hydroxide is then added drop by drop, the color of the solution changes to a bright red or pink. In the absence of other cations this test is sensitive in solution containing one part of stannous ion to two thousand parts of water. However, in the more dilute solutions it is always advisable to compare the solution with a blank, otherwise the slight color change cannot be detected. It should be noted that this test is not based upon the adsorption of the dye by a precipitate as in the two fluorescein tests which have been described.

Obviously, this test would be of no value in the presence of metals whose hydroxides are easily reduced to the colloidal metallic state by the sodium stannite present. This is true in such cases as silver, mercurous, mercuric, and bismuth. Neither will it be of much value in the presence of the colored ions. A striking exception is seen, though, in the case of a dilute copper solution where a good orange color appears. It seems to work satisfactorily in the presence of all other ions except that some care must be exercised in those cases where a heavy precipitate is formed. However, in the case of a heavy precipitate of lead chloride the color test is quite sensitive. In the presence of manganese the color is more of a violet, while with magnesium it is of an orchid tinge. The same test may be observed by using ammonium hydroxide or sodium carbonate, although it seems to be more delicate in the presence of sodium hydroxide.



STILL FOR THE PREPARATION OF BRANDY

Wood-cut from the *Coelum Philosophorum, seu Liber de Secretis Naturae* (Heaven of the Philosophers, or Book of the Secrets of Nature) of Philip Ulstadius, Leiden, 1572.

ELEMENTS *of the* QUANTUM THEORY*

VIII. PERTURBATION THEORY

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INTRODUCTORY REMARKS

THE problem of the atom with more than one electron is one which, on the basis of the Bohr theory, has its analog in celestial mechanics, where the problem is that of calculating, for instance, the effect of the gravitational pull of the sun on the motion of the moon around the earth. The field due to the action of the sun is said "to perturb" the motion of the moon, and obviously the effect of the sun must vary with its position in relation to both the moon and earth.

It is the existence of similar perturbations in atomic systems due to the interaction of the electrons that makes the consideration of such systems a more complex mathematical problem than that of the hydrogen-like atom. Thus, in the case of the helium atom, the simplest type of many-electron atoms, the total energy is evidently made up of three terms:

(1) the kinetic energy of each electron,
(2) the potential energy due to the *attractive* force between the nucleus and each electron,
(3) the potential energy due to the *repulsive* force between electrons.

If we designate the charge on the helium-like nucleus by Ze, the distance of each electron from the nucleus by r_1 and r_2, respectively, and the interelectronic distance by r_{12}, the total potential energy term is given by

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

The corresponding S. equation is given by

$$\nabla^2_1\phi + \nabla^2_2\phi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right)\phi = 0 \quad (279)$$

where the subscripts 1 and 2 of the Laplacian operators (in *polar coördinates*) refer to each electron. If the term e^2/r_{12} were omitted, the solution of the S. equation would be identical with that for two *separate* hydrogen-like atoms of nuclear charge, Ze. That is, the solution would be

$$\phi = \phi_{n_1l_1m_1}(r_1,\theta_1,\eta_1)\cdot\phi_{n_2l_2m_2}(r_2,\theta_2,\eta_2) \quad (280)$$

where r, θ, and η, are the coördinate variables of each electron with respect to each nucleus, and ϕ is a characteristic function of the form dealt with previously in discussing the hydrogen-like system. Furthermore, the characteristic energy values would be given by

$$E = E_{n_1} + E_{n_2}$$

where E_{n_1} and E_{n_2} represent the eigenvalues corresponding to the functions ϕ_{n_1} and ϕ_{n_2}, respectively.

It is the presence of the "perturbation" potential energy term, e^2/r_{12}, which makes the solution of the S. equation (279) more difficult. A similar perturbation term occurred in the S. equation (260) for the interaction of two linear harmonic oscillators, and there the mathematical difficulty was overcome by a transformation of coördinates. By this process it was found possible to separate the variables and thus obtain a product solution of the form indicated in (280). However, it has not been found possible to devise a transformation scheme for equation (279), by which the variables may be separated.

Consequently, it is necessary to use other methods. Of these the most important are the application of the perturbation theory, and a method based on the calculus of variations. It should be mentioned that the first of these represents the quantum mechanics modification of the method which has been used in calculations of orbits in celestial mechanics, while the second method involves a fundamental principle which has also been applied in classical physics.

The perturbation theory has been described by E. C. Kemble, as "Mostly machinery—a necessary evil!" The derivation of the first- and second-order perturbation terms given in the following sections is practically the same as that given by Condon and Morse.† It has the advantage over the derivation given by Schroedinger and other writers in the fact that it requires no knowledge of Green's theorem.

In the following sections an attempt has been made to present each of the steps in the derivation as clearly as possible, and for this reason the whole argument will appear somewhat tedious at best. However, the only excuse that can be given for the whole discussion is that a knowledge of the perturbation theory and of the accompanying concept of matrix elements is absolutely essential for the proper understanding of the manner in which quantum mechanics has solved a vast number of problems presented by atomic and molecular systems.

PERTURBATION THEORY—FIRST-ORDER TERMS

Let us consider first the non-degenerate case, that

* This is the tenth of a series of articles presenting a more detailed and extended treatment of the subject matter covered in Dr. Dushman's contribution to the symposium on Modernizing the Course in General Chemistry conducted by the Division of Chemical Education at the eighty-eighth meeting of the American Chemical Society, Cleveland, Ohio, September 12, 1934. The author reserves the right to publication in book form.

† CONDON AND MORSE, "Quantum mechanics," Chapter IV.

is, one in which there is only one eigenfunction corresponding to each discrete energy state. The S. equation for a given system will be of the form

$$\nabla^2 u + \alpha^2 (E - V)u = 0 \qquad (281)$$

where $\alpha^2 = 8\pi^2\mu/h^2$, and $\nabla^2 u$ may be of the form $\nabla_1{}^2 u + \nabla_2{}^2 u + \ldots$, if we are considering an atomic system containing two or more electrons. The potential energy, V, is of the form

$$V = V_0 + \lambda V_1 \qquad (282)$$

where V_0 represents the potential energy in the absence of any perturbation, while λV_1 is the perturbation term. We regard the latter as the product of a term V_1 which depends upon the coördinates and an abitrary parameter, λ, the value of which is small. Thus in the case of the helium-like atom, we could write

$$\frac{V}{Z} = -\left(\frac{e^2}{r_1} + \frac{e^2}{r_2}\right) + \frac{e^2}{Zr_{12}}$$

and regard $1/Z$ as such a variable parameter whose value would be small for large values of Z.

The S. equation for the unperturbed system is of the form

$$\nabla^2 u + \alpha^2(E - V_0)u = 0 \qquad (283a)$$

and we shall assume that solutions of this equation are known. We shall designate these by $u_n{}^0$ and the corresponding eigenvalues by $E_n{}^0$, so that they satisfy the S. equation:

$$\nabla^2 u^0{}_n + \alpha^2(E_n{}^0 - V_0)u_n{}^0 = 0 \qquad (283b)$$

Furthermore, we shall assume that these functions $u_n{}^0$, which form an orthogonal system, are also normalized.* That is,

$$\int \bar{u}_n{}^0 u_m{}^0 d\tau = \delta_{nm} = \begin{cases} 0 \text{ for } n \neq m \\ 1 \text{ for } n = m \end{cases} \qquad (284)$$

where $d\tau$ indicates the element of "volume" (which in the case of an atomic system will be of dimension 3ν, if ν represents the total number of electrons), and the integration is carried out over the whole domain in which the coördinate variables have a physical significance. The symbol δ_{nm} is used generally in quantum mechanics in order to indicate that the expression may have the value 1 or 0 according as n is equal or not, to m, and we shall, henceforth, use it in the sense defined in equation (284).

Let us now assume that the functions and energy values which are obtained by solving the S. equation (281), for the perturbed system, may be represented in terms of the functions $u_n{}^0$ and $E_n{}^0$ by expressions of the form

$$u_n = u_n{}^0 + \lambda\phi_n + \lambda^2\chi_n \qquad (285a)$$

$$E_n = E_n{}^0 + \lambda\epsilon_n + \lambda^2\eta_n \qquad (285b)$$

where ϕ_n and χ_n are functions of the coördinate variables, which represent the first-order and second-order perturbations, respectively, while ϵ_n and η_n represent the corresponding perturbation energy terms of the first and second order, respectively. The parameter λ is identical with that used in equation (282).

If, now, we replace V, u, and E in equation (281) by the expressions in equations (282), (285a), and (285b), respectively, and carry out the multiplication indicated, the resultant equation is of the form,

$$\begin{aligned}(1/\alpha^2)\ &\{\nabla^2 u_n{}^0 + \lambda\nabla^2\phi_n + \lambda^2\nabla^2\chi_n\} \\ &+ E_n{}^0 u_n{}^0 + \lambda E_n{}^0\phi_n + \lambda^2 E_n{}^0\chi_n \\ &- V_0 u_n{}^0 - \lambda V_0\phi_n - \lambda^2 V_0\chi_n \\ &+ \lambda\epsilon_n u_n{}^0 + \lambda^2\epsilon_n\phi_n \\ &- \lambda V_1 u_n{}^0 - \lambda^2 V_1\phi_n \\ &- \lambda^2\eta_n u_n = 0 \end{aligned} \qquad (286)$$

Since λ is an arbitrary parameter, it follows that the coefficient of each power of λ in equation (286) must vanish identically. The coefficient of $\lambda^0 = 1$ is evidently the same as the left-hand side of equation (283b) and merely states the obvious conclusion that for $\lambda = 0$, the solutions of equations (283a) and (281) are identical.

The coefficient of λ in equation (286) yields the *inhomogeneous* differential equation,

$$\nabla^2\phi_n + \alpha^2(E_n{}^0 - V_0)\phi_n = \alpha^2(V_1 - \epsilon_n)u_n{}^0 \qquad (287)$$

If the right-hand side of this equation were equal to zero, the equation would be of *homogeneous* type and identical in form with equation (283b). The presence of the expression on the right-hand side of (287) necessitates a special procedure in order to solve the equation.

Since ϕ_n is assumed to be a function of the coördinate variables which is finite and continuous over the whole domain, it may be expressed as a "Fourier's series" in terms of the orthonormalized functions $u_k{}^0$. That is, it is possible to develop the function ϕ_n in the form

$$\phi_n = \sum_k B_{nk} u_k{}^0 \qquad (288)$$

where the summation is extended over all integral values of k from 0 to ∞, and any one of the coefficients B_{nk} could be derived by the relation

$$B_{nk} = \int \bar{u}_k{}^0 \phi_n d\tau$$

as indicated in Appendix III.† However, we shall leave the coefficients undetermined for the present. The subscript nk indicates that the coefficient is that of the function $u_k{}^0$ and furthermore that it refers to the series development for the function ϕ_n. Thus, for each characteristic solution, u_n of the S. equation, there will exist a function ϕ_n which may be represented by an infinite series of terms, each of which is the product of a constant (that is, a magnitude such as B_{nk} which is independent of the coördinate variables) and one of the series of orthonormal functions $u_n{}^0$.

Substituting from (288) into (287), the result is

$$\sum_k B_{nk}\nabla^2 u_k{}^0 + \alpha^2 \sum_k B_{nk}(E_n{}^0 - V_0)u_k{}^0 = \alpha^2(V_1 - \epsilon_n)u_n{}^0 \qquad (289)$$

But, according to equation (283b),

* Such functions have been designated as *orthonormal*.

† J. CHEM. EDUC., **12**, 490–1 (Oct., 1935).

$$\nabla^2 u_k^0 - \alpha^2 V_0 u_k^0 = -\alpha^2 E_k^0 u_k^0$$

Hence equation (289) may be written in the form

$$\sum_k B_{nk}(E_n^0 - E_k^0)u_k^0 = (V_1 - \epsilon_n)u_n^0 \qquad (290)$$

Multiplying both sides of (290) by $\bar{u}_n^0$ and integrating over the complete domain of the coördinate variables (or configuration space), the result is

$$\sum_k B_{nk}(E_n^0 - E_k^0)\int \bar{u}_n^0 u_k^0 d\tau = \int \bar{u}_n^0 V_1 u_n^0 d\tau - \epsilon_n \int \bar{u}_n^0 u_n^0 d\tau \qquad (291)$$

Since ϵ_n is a constant (the perturbation energy of the first order), it may be written outside the sign of integration, whereas V_1 must be kept inside the integration sign because it is a function of the coördinate variables.

Now for $k = n$, $E_n^0 - E_k^0 = 0$, while for $k \neq n$, $\int \bar{u}_n^0 u_k^0 d\tau = 0$. On the other hand, since u_n^0 is a normalized function,

$$\int \bar{u}_n^0 u_n^0 d\tau = 1.$$

Hence, we deduce from (291) the very important result,

$$\epsilon_n = \int \bar{u}_n^0 V_1 u_n^0 d\tau \qquad (292a)$$

"Thus," as Condon and Morse remark,* "the linear correction to any energy level is simply the average value of the linear term in the potential energy function weighted according to the value of the squared characteristic function at each place. This theorem is the quantum mechanical analog of a similar result in classical mechanics: *The alteration of the energy of a quantum state in the first approximation is equal to the average of the perturbation potential taken over the undisturbed orbit.*"

If u_n^0 is a real function, equation (292*a*) becomes

$$\epsilon_n = \int (u_n^0)^2 V_1 d\tau \qquad (292b)$$

in which the "squared characteristic function" takes the place of the real magnitude $\bar{u}_n^0 u_n^0$ in (292*a*).

We may now proceed to determine the coefficients B_{nk} in the expansion for ϕ_n, as given by equation (288). If in equation (290) we multiply through by $\bar{u}_j^0$ and integrate over the configuration space, we obtain the relation

$$\sum_k B_{nk}(E_n^0 - E_k^0)\int \bar{u}_j^0 u_k^0 d\tau = \int \bar{u}_j^0 V_1 u_n^0 d\tau - \epsilon_n \int \bar{u}_j^0 u_n^0 d\tau$$

Because of the orthogonality relation (284), the only non-vanishing term on the left-hand side is that for which $k = j$, while the coefficient of ϵ_n will vanish for $j \neq n$. Hence

$$B_{nj} = \frac{\int \bar{u}_j^0 V_1 u_n^0 d\tau}{(E_n^0 - E_j^0)} \qquad (293)$$

where $j \neq n$.

To determine the value of B_{nn}, we make use of the requirement that u_n, the perturbed eigenfunction, must also be a normalized function. Hence

$$\int \bar{u}_n u_n d\tau = 1 = \int \bar{u}_n^0 u_n d\tau + \lambda \int \bar{u}_n^0 \phi_n d\tau + \lambda \int u_n^0 \bar{\phi}_n d\tau + \lambda^2 \int \bar{\phi}_n \phi_n d\tau + \lambda^2 \int \bar{u}_n^0 \chi_n d\tau + \lambda^2 \int u_n^0 \bar{\chi}_n d\tau + \ldots$$

Because of the validity of equation (284) it follows that

$$0 = \lambda\left(\int \bar{u}_n^0 \phi_n d\tau + \int u_n^0 \bar{\phi}_n d\tau\right) + \text{terms in higher powers of } \lambda.$$

Since λ is a variable parameter, each power of λ must vanish identically, and using the series for ϕ_n it follows that

$$\int \bar{u}_n^0 \left(\sum_k B_{nk} u_k^0\right) d\tau + \int u_n^0 \left(\sum_k B_{nk} \bar{u}_k^0\right) d\tau = 0$$

In this equation, however, each term, except that for which $k = n$, vanishes because of the orthogonality relation (since B_{nk} may be written outside the sign of integration for each term). Consequently

$$2B_{nn}\int \bar{u}_n^0 u_n d\tau = 0$$

and hence, $B_{nn} = 0$.

That is, the series for ϕ_n is of the form

$$\phi_n = \sum_k{}' \frac{H_{kn}}{E_n^0 - E_k^0} \cdot u_k^0 \qquad (294)$$

where the prime over the summation sign indicates that the value $k = n$ is *excluded* in the summation, and

$$H_{kn} = \int \bar{u}_k^0 V_1 u_n^0 d\tau \qquad (295)$$

The quantity H_{kn} has been designated, for reasons which will be discussed in a subsequent section, as a "*matrix element*," and in the following remarks this designation, as well as the symbol H_{nk}, will be used to represent integrals of the type shown in equation (295).

In this connection it is also necessary to point out that unless V_1 possesses the properties of an operator, the expression $\bar{u}_n^0 u_k^0 V_1$ is identical with $\bar{u}_n^0 V_1 u_k^0$. However, in view of the fact that in many quantum mechanical problems the matrix elements contain operators which play the same rôle as V_1 (but which are non-commutative), the order of the factors in any one element becomes of prime importance. For this reason it has been considered advisable in the consideration of matrix elements such as H_{kn}, or ϵ_n, to write the expressions for the integrands in the form used in (292*a*) and (295) rather than in that used in (292*b*), even when V_1 may be commuted with the functions $\bar{u}_n^0 u_k^0$ or $\bar{u}_n^0 u_n^0$.

* CONDON AND MORSE, "Quantum mechanics," p. 119.

SECOND-ORDER PERTURBATION TERMS

To calculate the *second-order* perturbation terms, η_n and χ_n, it is necessary to consider the inhomogeneous differential equation obtained from equation (286) by equating the coefficient of λ^2 to zero. The resulting equation has the form

$$(1/\alpha^2)\Delta\chi_n + (E_n^0 - V_0)\chi_n = \eta_n u_n^0 - (\epsilon_n - V_1)\phi_n \quad (296)$$

As in the calculation of the first-order perturbation terms, we assume that χ_n may be represented by a Fourier's series expansion in terms of the orthogonal and normalized functions u_n^0. That is, we assume

$$\chi_n = \sum C_{nk} u_k^0 \quad (297)$$

where the coefficients C_{nk} of each term will have to be determined by a procedure analogous to that used for the determination of the coefficients B_{nk} in the series for ϕ_n.

Substituting (297) in (296), the result is

$$\sum_k C_{nk}\left\{(1/\alpha^2)\nabla^2 u_k^0 - V_0 u_k^0 + E_n^0 u_k^0\right\} = \eta_n u_n^0 - (\epsilon_n - V_1)\phi_n$$

But

$$(1/\alpha^2)\nabla^2 u_k^0 - V_0 u_k^0 = -E_k^0 u_k^0$$

Hence

$$\sum_k C_{nk}(E_n^0 - E_k^0)u_k^0 = \eta_n u_n^0 - (\epsilon_n - V_1)\phi_n \quad (298)$$

Multiplying both sides of (298) by $\bar{u}_n^0$ and integrating, it follows from considerations similar to those used in deriving the value of ϵ_n that

$$\begin{aligned}\eta_n &= -\int \bar{u}_n^0(V_1 - \epsilon_n)\phi_n d\tau \\ &= -\sum_k{}' B_{nk}\int \bar{u}_n^0(V_1 - \epsilon_n)u_k^0 d\tau \\ &= -\sum_k{}' \frac{H_{kn}}{(E_n^0 - E_k^0)}\int \bar{u}_n^0(V_1 - \epsilon_n)u_k^0 d\tau \\ &= -\sum_k{}' \frac{H_{kn}}{(E_n^0 - E_k^0)}\int u_n^0 V_1 u_k^0 d\tau \\ &= -\sum_k{}' \frac{H_{kn}\cdot H_{nk}}{(E_n^0 - E_k^0)} \end{aligned} \quad (299)$$

where H_{nk} is a matrix element defined by equation (295).

The method used for the determination of the second-order perturbation function, χ_n, is similar to that involved in the derivation of the first-order term, ϕ_n.

From equation (298), by using the series for ϕ_n, it follows that

$$\sum_k C_{nk}(E_n^0 - E_k^0)u_k^0 = \eta_n u_n^0 + \sum_j{}' B_{nj} V_1 u_j^0 - \epsilon_n \sum_j{}' B_{nj} u_j \quad (300)$$

(The subscript j is used to differentiate the members of the series from the series on the left-hand side.)

Multiplying both sides of equation (300) by $\bar{u}_i^0$ (where i is one of the series of values, 1, 2....j...k...), and integrating over the whole domain of the coördinate variables, we obtain the relation

$$C_{ni}(E_n^0 - E_i^0) = \sum_j{}' B_{nj}\int \bar{u}_i^0 V_1 u_j^0 d\tau - \epsilon_n \sum_j{}' B_{nj}\int \bar{u}_i^0 u_j^0 d\tau \quad (301)$$

since the terms on the left-hand side of (300) which do not involve E_i^0 vanish, while on the right-hand side the term involving η_n vanishes since $i \neq n$.

Now in (301)

$$\int \bar{u}_i^0 u_j^0 d\tau = \delta_{ij} = \begin{cases} 1 \text{ for } j = i \\ 0 \text{ for } j \neq i \end{cases}$$

also for $j = i$

$$\int \bar{u}_i^0 V_1 u_j^0 d\tau = \epsilon_i$$

while for $j \neq i$

$$\int \bar{u}_i^0 V_1 u_j^0 d\tau = H_{ij}$$

Substituting these relations as well as that for B_n from equations (293) and (294), it follows that

$$C_{ni} = \frac{(\epsilon_i - \epsilon_n)H_{in}}{(E_n^0 - E_i^0)^2} + \sum_j{}'' \frac{H_{ij}\cdot H_{jn}}{(E_n^0 - E_i^0)(E_n^0 - E_j^0)} \quad (302)$$

where the two primes over the summation sign indicate that the two values $j = i$ and $j = n$ are *excluded*. It may be shown that the requirement of normalization for the function u_n leads in this case (as in the case of the coefficients B_{nj}) to the conclusion $C_{nn} = 0$.

PERTURBATION TERMS IN RELATION TO MATRIX ELEMENTS

It is important for an understanding of the "language" used in discussing problems in quantum mechanics to consider the relationships of the various perturbation terms derived in the previous sections to matrix elements. Furthermore, such remarks will form an introduction to the more detailed discussion of matrices which will form the topic of a subsequent chapter.

A matrix is defined as an *array* of magnitudes in rows and columns. It is merely a table in which certain elements are arranged according to a definite order.

A very simple type of matrix is obtained from a consideration of three linear equations in x, y, z of the form

$$\begin{aligned} a_1 x + b_1 y + c_1 z &= 0 \\ a_2 x + b_2 y + c_2 z &= 0 \\ a_3 x + b_3 y + c_3 z &= 0 \end{aligned}$$

These three equations will yield definite values of x, y, and z if the *determinant*

$$\begin{vmatrix} a_1b_1c_1 \\ a_2b_2c_2 \\ a_3b_3c_3 \end{vmatrix} = 0$$

The *array* of values

$$\begin{pmatrix} a_1b_1c_1 \\ a_2b_2c_2 \\ a_3b_3c_3 \end{pmatrix}$$

indicated by round brackets is known as a matrix.

More generally, if we have n equations in the n variables $x_1, x_2, \ldots x_n$, these will be of the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \ldots\ldots\ldots + a_{1n}x_n &= 0 \\ a_{21}x_1 + a_{22}x_2 + \ldots\ldots\ldots + a_{2n}x_n &= 0 \\ \ldots\ldots\ldots\

$$u'_{n\mu} = \sum_{\gamma} C_{\mu\gamma} u_{n\gamma}{}^0 \tag{304}$$

where $C_{\mu\gamma}$ is a coefficient the value of which varies with that of γ and also depends upon the value of μ. Each series on the right-hand side of (304) contains ν-terms corresponding to the ν-function $u_{n\mu}{}^0$ (or $u_{n\gamma}{}^0$).

Hence, the first-order approximation to the eigenfunction for the perturbed state is given by

$$u_{n\mu} = u_{n\mu}' + \lambda\phi_{n\mu} \tag{305}$$

where $\phi_{n\mu}$ plays a rôle similar to that of ϕ_n in equation (285a).

The S. equation for the perturbed states is given by

$$\nabla^2(u_{n\mu}' + \lambda\phi_{n\mu}) + \alpha^2(E_n{}^0 + \lambda\epsilon_{n\mu} - V_0 - \lambda V_1)(u_{n\mu}' + \lambda\phi_{n\mu}) = 0$$

It follows that

$$\nabla^2 u_{n\mu}' + \alpha^2(E_n{}^0 - V_0)u_{n\mu}' = 0 \tag{306}$$

also that

$$\nabla^2\phi_{n\mu} + \alpha^2(E_n{}^0 - V_0)\phi_{n\mu} = \alpha^2(V_1 - \epsilon_{n\mu})u_{n\mu}' \tag{307}$$

Evidently equation (306) is satisfied because of the validity of equation (304). To determine ϵ_n we proceed by assuming that $\phi_{n\mu}$ can also be developed in terms of the unperturbed functions $u_{k\beta}{}^0$ in the form

$$\phi_{n\mu} = \sum_k \sum_\beta A_{k\beta} u_{k\beta}{}^0 \tag{308}$$

where the values of the coefficients $A_{k\beta}$ will depend upon the particular values of n and μ as well as on k and β. The notation $u_{k\beta}{}^0$ refers to any one of the set functions which correspond to the same energy state $E_k{}^0$.

Substituting from equation (308) in equation (307), the result is

$$\sum_k \sum_\beta A_{k\beta}(E_n{}^0 - E_k{}^0)u_{k\beta}{}^0 = (V_1 - \epsilon_n)u_{n\mu}'$$

where ϵ_n is written instead of $\epsilon_{n\mu}$.

Multiplying both sides by $\bar{u}_{k\beta}{}^0$ and integrating over the whole domain, it is seen that

$$A_{k\beta}(E_n{}^0 - E_k{}^0) = \int \bar{u}_{k\beta}{}^0(V_1 - \epsilon_n)u_{n\mu}'\,d\tau$$

For $k = n$

$$0 = \int \bar{u}_{n\beta}{}^0(V_1 - \epsilon_n)u_{n\mu}'\,d\tau$$

By substituting for $u_{n\mu}'$ from equation (304), it follows that

$$\begin{aligned} 0 &= \sum_\gamma C_{\mu\gamma} \bar{u}_{n\beta}{}^0(V_1 - \epsilon_n)u_{n\gamma}{}^0 d\tau \\ &= \sum_\gamma C_{\mu\gamma}\left[\int \bar{u}_{n\beta}{}^0 V_1 u_{n\gamma}{}^0 d\tau - \epsilon_n \int \bar{u}_{n\beta}{}^0 u_{n\gamma}{}^0 d\tau\right] \\ &= \sum_\gamma C_{\mu\gamma}\left(H_{\beta\gamma}^{(n)} - \epsilon_n \delta_{\beta\gamma}^{(n)}\right) \end{aligned} \tag{309}$$

where

$$H_{\beta\gamma}^{(n)} = \int \bar{u}_{n\beta}{}^0 V_1 u_{n\gamma}{}^0 d\tau \tag{310a}$$

and

$$\delta_{\beta\gamma}^{(n)} = \int \bar{u}_{n\beta}{}^0 u_{n\gamma}{}^0 d\tau = \begin{cases} 0 \text{ for } \beta \neq \gamma \\ 1 \text{ for } \beta = \gamma \end{cases} \tag{310b}$$

For each value of β there will exist a relation similar to equation (309), and if there are ν eigenfunctions $u_{n\beta}{}^0$ (or $u_{n\gamma}{}^0$, $u_{n\mu}{}^0$, etc.) corresponding to the same energy value $E_n{}^0$ in the degenerate case, there will be obtained ν linear equations in the ν coefficients $C_{\mu\gamma}$, where $\gamma = 1, 2, \ldots\ldots \nu$. Each of these equations will be of the form

$$C_{\mu 1}(H_{\beta 1} - \epsilon_n\delta_{\beta 1}) + C_{\mu 2}(H_{\beta 2} - \epsilon_n\delta_{\beta 2}) + \ldots + C_{\mu\gamma}(H_{\beta\nu} - \epsilon_n\delta_{\beta\nu}) = 0$$

The ν equations thus constitute a system for the determination of the ν constants $C_{\mu 1}$, $C_{\mu 2}$, etc. The condition that such a system have a solution (other than the trivial one that each coefficient vanish identically) is that the determinant of the coefficients of these constants should vanish. That is, the condition is of the form,

$$\begin{vmatrix} H_{11} - \epsilon_n, & H_{12}, & H_{13}, \ldots . H_{1\nu} \\ H_{21}, & H_{22} - \epsilon_n, & H_{23}, \ldots . H_{2\nu} \\ H_{31}, & H_{32}, & H_{33} - \epsilon_n \ldots . H_{3\nu} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{\nu 1}, & H_{\nu 2}, & H_{\nu 3}, \ldots . H_{\nu\nu} - \epsilon_n \end{vmatrix} = 0 \tag{311}$$

where it will be observed that owing to the validity of equation (310b) the only coefficients of ϵ_n in equation (309) which are not identically equal to zero are those which are situated on the diagonal of the determinant in (311).

The order of the determinant in (311) is evidently the same as the order of degeneracy of the state for which the energy is $E_n{}^0$. Consequently, the equation for ϵ_n will be of the form

$$a_n\epsilon_n{}^\nu + a_{n-1}\epsilon_n{}^{\nu-1} + \ldots\ldots + a_0 = 0 \tag{312}$$

That is, it will be an algebraic equation in $\epsilon_n{}^\nu$, and will possess ν roots.

Equation (311) or (312) is known as the *secular equation*. That the roots are real is evident from the consideration that in the case of real functions $H_{\beta\gamma} = H_{\gamma\beta}$, while in the case of complex conjugate functions it may be demonstrated as in the case of the elements in equation (294) that $H_{\beta\gamma}$ and $H_{\gamma\beta}$ constitute a *complex conjugate pair*.

An illustration of the application of the secular equation to the case, $\nu = 2$, will be given in the following chapter in the discussion of the helium atom problem.

Having determined the ν different values of ϵ_n, it becomes possible to obtain *for each of these values* a solution of the set of equations (309) for the ratios of the C's. In other words, for each value, $\epsilon_{n\mu}$, a set of values of the ratios of the coefficients $C_{\mu 2}|C_{\mu 1}$; $C_{\mu 3}|C_{\mu 1}$; $\ldots\ldots\ldots$ $C_{\mu\nu}|C_{\mu 1}$ is obtained, from which the expansion indicated in equation (304) for $u_{n\mu}'$ may be written out.

The procedure for the determination of the coefficients $A_{k\beta}$ in (308) is similar to that used in the non-degenerate case, but more tedious. The relation for $u_{n\mu}$ is of the form

$$u_{n\mu} = \sum_{\gamma} C_{\mu\gamma} \left\{ u_{n\gamma}{}^{0} + \lambda \sum_{k} \sum_{\beta} \frac{\int \bar{u}_{k\beta}{}^{0} V_1 u_{n\gamma}{}^{0} d\tau}{E_n{}^{0} - E_k{}^{0}} \right\} \quad (313)$$

where the summation inside the brackets extends over all states for which $k \neq n$.

APPLICATION TO COUPLED LINEAR OSCILLATORS

As mentioned at the beginning of this chapter, the perturbation theory is essentially a method of transformation by means of which the solution for the perturbed energy state is expressed in terms of the known solution for the unperturbed state and of the expression for the perturbing potential energy function.

It is therefore of interest to consider the solution by the perturbation theory method of a problem for which the solution may also be derived by means of a transformation of coördinate variables. Such a problem is that of the coupled linear harmonic oscillators considered in Chapter VII. The S. equation for the system as shown in that connection is of the form,

$$\frac{\partial^2\phi}{\partial q_1{}^2} + \frac{\partial^2\phi}{\partial q_2{}^2} + \alpha^2 \left(E - \frac{kq_1{}^2}{2} - \frac{kq_2{}^2}{2} + \frac{2e^2 q_1 q_2}{R^3} \right)\phi = 0 \quad (260)$$

where $\alpha^2 = 8\pi^2\mu/h^2$ and q_1 and q_2 refer to the coördinates of each particle, measured along the same coördinate axis.

It was shown that this equation could be transformed by a change of the variables to the so-called "normal" form, so that the resulting characteristic function could be expressed as the product of two functions (each a function of only one variable). In this case the perturbation term in the expression for the potential energy function is given by $2e^2q_1q_2/R^3$, and it was found that this leads to a perturbation term in the expression for the total energy of the form,

$$\Delta E = -\frac{h\nu_0 e^4}{2k^2R^6} \quad (267)$$

which corresponds to an attractive force between the oscillating particles.

Let us now consider the same problem from the point of view of the perturbation theory.

Using the same symbols as in the problem of the linear harmonic oscillator (see Chapter IV), the frequency of each identical oscillator in the unperturbed state is given by

$$\nu_0 = \sqrt{k/\mu}/2\pi .$$

We shall replace q_1 and q_2 in equation (260) by the new variables x_1 and x_2, respectively, defined by the relation

$$\left.\begin{aligned} x = q\sqrt{b} &= q \cdot 2\pi\sqrt{\mu\nu_0/h} \\ &= q \cdot \sqrt{k/(h\nu_0)} \end{aligned}\right\} \quad (110)$$

Consequently, equation (260) becomes

$$\frac{\partial^2\phi}{\partial x_1{}^2} + \frac{\partial^2\phi}{\partial x_2{}^2} + \left(\frac{a}{b} - x_1{}^2 - x_2{}^2 + \lambda x_1 x_2 \right)\phi = 0 \quad (314)$$

where

$$\left.\begin{aligned} a &= 8\pi^2\mu E/h^2 \\ \lambda &= \frac{16\pi^2\mu e^2}{h^2R^3} \cdot \frac{1}{b^2} = \frac{4e^2}{kR^3} \end{aligned}\right\} \quad (315)$$

Thus the perturbation potential energy term is $-\lambda x_1 x_2$ where λ is a parameter, the value of which vanishes for the unperturbed state ($R = \infty$).

The characteristic function for the unperturbed state is

$$u_{n,m}{}^{0} = \phi_n(x_1) \cdot \phi_m(x_2) \quad (316)$$

and the energy of the system for the quantum states, n and m of each oscillator, is

$$E^0{}_{n,m} = (n + 1/2)h\nu_0 + (m + 1/2)h\nu_0 = (n + m + 1)h\nu_0 \quad (317)$$

As shown in Chapter IV, the function $\phi_n(x)$ is real and has the form

$$\phi_n(x) = \epsilon^{-x^2/2} H_n(x)$$

where $H_n(x)$ is the Hermitian polynomial of the nth degree.

Applying equation (299a) for the first-order perturbation energy, which will be designated by $\Delta E^{(1)}$, it follows that

$$\Delta E^{(1)} = -\lambda \int (u_{nm}{}^{0})^2 \, x_1 x_2 dx_1 dx_2$$

where the limits of integration are $\pm\infty$ for each variable. Hence,

$$\Delta E^{(1)} = -\lambda \int \phi_n(x_1) x_1 dx_1 \int \phi_m(x_1) x_2 dx_2 \quad (318)$$

But as was shown in Chapter IV, the integrals on the right-hand side of (318) correspond to the average values of x_1 and x_2 respectively and each of these vanishes. Hence,

$$\Delta E^{(1)} = 0$$

Let us now consider the second-order perturbation energy. According to equation (299) this is given by the relation,

$$\Delta E^{(2)} = \lambda^2 \sum \frac{(H_{ij})^2}{(E_{n,m}{}^{0} - E_{n',m'}{}^{0})} \quad (319)$$

where

$$H_{ij} = -\int u_{nm}{}^{0} x_1 x_2 u_{n'm'}{}^{0} dx_1 dx_2 \quad (320)$$

and n' and m' correspond to the values of the quantum numbers n and m for any other state of the system. Thus the total energy of the oscillators in the state $n'm'$ is given by

$$E_{n'm'}{}^{0} = (n' + m' + 1)h\nu_0$$

Evidently,

$$H_{ij} = -\int \phi_n(x_1)\phi_{n'}(x_1) x_1 dx_1 \int \phi_m(x_2)\phi_{m'}(x_2) x_2 dx_2$$

and the summation in (318) is extended over all possible values of n' and m', excluding the state $n' = n$, $m' = m$.

Now for the oscillators under consideration, $n = m = 0$. Also, as shown in Chapter IV [see equation (139a) and subsequent discussion], the integral

$$I_{n,n'} = \int \phi_n(x)\,\phi_{n'}(x)\,x dx$$

vanishes unless $n' - n = \pm 1$. Since $n = 0$, the only possible value of n' is 1, and similarly for m'. Furthermore, since

$$I_{1,0} = \sqrt{1/2}$$

it follows that

$$H_{ij} = -(1/\sqrt{2})(1/\sqrt{2}) = -1/2$$

and

$$(H_{ij})^2 = 1/4.$$

This constitutes the only term in the summation indicated in equation (319). To determine the corresponding values of the denominator $E_{00} = E_{11}^0$, it must be observed that in equation (314) both a/b and x are *dimensionless*, and hence in equation (319) $\Delta E^{(2)}$ is expressed as a multiple of a unit of energy. Since $a/b = 2E/h\nu_0$, the unit of energy is $h\nu_0/2$. In terms of these units,

$$E_{00} - E_{11}^0 = -2h\nu_0/(h\nu_0/2) = -4$$

Consequently,

$$\Delta E^{(2)} = -\frac{\lambda^2}{16}\left(\frac{h\nu_0}{2}\right) = -\left(\frac{4e^2}{kR^3}\right)^2 \cdot \frac{h\nu_0}{32} = -\frac{h\nu_0 e^4}{2k^2R^6} \qquad (321)$$

which is identical with the result obtained in equation (267), Chapter VII.

In order to obtain the corresponding perturbation terms in the eigenfunction for the system a much more tedious calculation is necessary, and hence the method used in Chapter VII is much more convenient in that respect. It should, however, be pointed out that while $\Delta E^{(1)}$ vanishes, it does not necessarily follow that the corresponding first-order perturbation term in the eigenfunction also vanishes. Thus, if we apply equation (294) we obtain the result

$$\Delta u^{(1)} = -\lambda u_{11}^0 \cdot \frac{\int \phi_0(x_1)\phi_1(x_1)x_1 dx_1 \int \phi_0(x_2)\phi_1(x_2)x_2 dx_2}{E_{00}^0 - E_{11}^0}$$

$$= -\frac{\lambda \cdot \phi_1(x_1)\phi_1(x_2)}{8}$$

$$= -(\lambda/2)\epsilon^{-(x_1^2 + x_2^2)/2} \cdot x_1 x_2$$

since $\phi_1(x) = 2x \cdot \epsilon^{-x^2/2}$.

Hence, to a first approximation, the eigenfunction for the system will be given by

$$u = \epsilon^{-(x_1^2 + x_2^2)/2}\left(1 - \frac{\lambda x_1 x_2}{2}\right)$$

$$= u_{00}\left(1 - \frac{\lambda x_1 x_2}{2}\right)$$

which shows that u will be greater or less than u_{00} according as $x_1 x_2$ is positive or negative.

In Chapter VII, as stated in that connection, the problem of the interaction of two hydrogen atoms at such a distance that there is no interchange of electrons was treated as a problem of three linear oscillators, each acting along one of the three orthogonal coördinate-axes. This is the method used by F. London* and also by J. E. Lennard-Jones.†

On the other hand, R. Eisenschitz and F. London‡ have applied the second-order perturbation theory, using for this purpose the wave functions for the hydrogen atom. This method has the advantage that it makes it possible to define more precisely the fictitious frequency ν_0 and also to determine the polarizability from dispersion theory.

APPLICATION OF PERTURBATION THEORY TO STARK AND ZEEMAN EFFECTS

In presence of magnetic fields (Zeeman effect) or strong electric fields (Stark effect) spectral lines are resolved into components.** Since any spectral line is due to a transition between two energy states, the observed effects must be due to the perturbing effect of the field on the motion of the electron about the nucleus, in each of the two energy states.

A simple illustration of the Stark effect is the problem discussed in Chapter VII and in the previous section, which dealt with the effect on the energy states and eigenfunctions of a linear harmonic oscillator of the field due to an identical oscillator at a distance.

In the case of the hydrogen atom, the S. equation for the perturbed state in presence of an electric field of strength F applied in the direction of the z-axis is of the form

$$\nabla^2\phi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{r} - eFz\right)\phi = 0$$

As shown by E. Schroedinger††† and subsequent investigators, the solution of this equation gives a value for the first-order perturbation term in the energy which is proportional to F and a second-order term which is proportional to F^2. The formulas thus derived are found to be in very good agreement with the actual observations on the splitting up of the hydrogen lines in an electric field.

In the case of the Zeeman effect the first-order perturbation energy term is given by the same relation as was derived in the older theory, that is,

$$\Delta E^{(1)} = \left(\frac{eH}{4\pi\mu c}\right)mh$$

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* F. LONDON, *Z. physik. Chem.*, **B11**, 222 (1931)

† J. E. LENNARD-JONES, *Proc. Phys. Soc. London*, **43**, 461 (1931).

‡ R. EISENSCHITZ AND F. LONDON, *Z. Physik.*, **60**, 491 (1930).

** For description of these observations see F. K. RICHTMEYER'S "Introduction to modern physics," also H. S. TAYLOR'S "Treatise on physical chemistry," Chapter XVI.

††† E. SCHROEDINGER, *Ann. Physik.*, **80**, 437 (1926). See also CONDON AND MORSE, pp. 123–9.

where m may have any one of the integral values ranging between $-l$ and $+l$, and H is the strength of the magnetic field. It should be added in this connection that the reader will find a number of interesting illustrations of the application of the perturbation theory in the book by L. Pauling and E. B. Wilson, Jr., "Introduction to quantum mechanics," McGraw-Hill Book Co., Inc., New York, **1935**, Chapter VI.

MATHEMATICAL PROBLEM PAGE

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AN ORDINARY differential equation is a relation between the variables, x and y, and one or more of the derivatives, $\frac{dy}{dx}$, $\frac{d^2y}{dx^2}$, etc. The *order* of an equation is the order of the highest derivative which appears in it. The *degree* is the power to which this highest derivative is raised after the equation has been cleared of fractions and radicals. The general solution of a differential equation contains a number of arbitrary independent constants equal to the order of the equation. In most applications of differential equations to physical phenomena these constants can be evaluated for the conditions of the problem at hand.

First-order, first-degree equations have the form:

$$F_1(x,y) + F_2(x,y)(dy/dx) = 0$$

or $Mdx + Ndy = 0$, where $M = F_1(x,y)$ and $N = F_2(x,y)$. There are several methods for the solution of such equations. This month we shall consider only two types: (1) *The variables are separable.* The equation is either in the form that M is a function of x alone and N a function of y alone or it can be put in this form by slight manipulation. The solution is obtained by simple integration:

$$F_1(x)dx + F_2(y)dy = 0$$
$$\int F_1(x)dx + \int F_2(y)dy = C$$

(2) *The equation is homogeneous.* An equation is homogeneous with respect to x and y if the sum of the powers of x and y in each term is a constant. Thus, a homogeneous equation can contain no constant term. Such equations may be transformed into ones which are solvable by separation of the variables by the substitutions of $y = vx$ and $dy = vdx + xdv$.*

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PARTINGTON, "Higher mathematics for chemical students," 3rd ed., D. Van Nostrand Co., Inc., New York City, p. 214.

* An equation of the first degree with respect to y and x of the type:

$$(a'x+b'y+c')dy-(ax+by+c)dx=0$$

can be transformed into the homogeneous form by the substitution of $x-u+h$, $y=v+k$, $dx=du$ and $dy=dv$; h and k are chosen so that $ah+bk+c=0$ and $a'h+b'k+c'=0$.

PROBLEMS

1. Obtain a differential equation free from arbitrary constants for which $y = ax^2 + bx$ is a general solution.
2. Solve: $yxdx + xy^2dy = 0$

   $$(x^2 - yx^2)\,(dy/dx) + y^2 + xy^2 = 0$$
3. Solve: $x^2ydx - (x^3 + y^3)dy = 0$
4. Solve: $(3y - 7x + 7)dx + (7y + 3x + 3)dy = 0$
5. For the adiabatic expansion of a perfect gas ($pV = RT$) the differential equation is $pdV = -c_vdT$ where c_v is the heat capacity at constant volume and may be considered constant. Solve the equation. Show also that $pV^\gamma = \text{const.}$ where $\gamma = c_p/c_v$ and $c_p = c_v + R$.
6. Solve the differential equation for the velocity of a bimolecular reaction:

   $$dx/dt = k(a - x)\,(b - x)$$

   Evaluate the arbitrary constant from the fact that at $t = 0$, $x = 0$.

SOLUTIONS TO JANUARY PROBLEMS

1. $\partial u/\partial x = 3x^2y^2 - 4x^3y^2 - 3x^2y^3 = x^2y^2(3 - 4x - 3y)$
   $\partial^2u/\partial x^2 = 6xy^2 - 12x^2y^2 - 6xy^3 = xy^2(6 - 12x - 6y)$
   $\partial u/\partial y = 2x^3y - 2x^4y - 3x^3y^2 = x^3y(2 - 2x - 3y)$
   $\partial^2u/\partial y^2 = 2x^3 - 2x^4 - 6x^3y = x^3(2 - 2x - 6y)$
   $\partial^2u/(\partial x\partial y) = 6x^2y - 8x^3y - 9x^2y^2 = x^2y(6 - 8x - 9y)$
   $\partial u/\partial x = \partial u/\partial y = 0$ for the solution of the two simultaneous equations: $3 - 4x - 3y = 0$ and $2 - 2x - 3y = 0$.

   The solution is $x = {}^1/_2$ and $y = {}^1/_3$.

   Under these conditions $\frac{\partial^2u}{\partial x^2}$ is negative and $\frac{\partial^2u}{\partial x^2}\cdot\frac{\partial^2u}{\partial y^2} - \frac{\partial^2u}{\partial x\partial y}$ is greater than zero. Therefore $x = {}^1/_2$ and $y = {}^1/_3$ is a maximum point in the given function.
2. Let the number C be divided into three parts, x, y, and $(C - x - y)$. The problem requires the relationship between x and y when the function $u = xy(C - x - y)$ is at a maximum.

   $\frac{\partial u}{\partial x} = Cy - 2xy - y^2 = y(C - 2x - y)$; $\frac{\partial^2u}{\partial x^2} = -2y$

$\partial u/\partial y = Cx - x^2 - 2xy = x(C - x - 2y)$
$\partial^2 u/(\partial x \partial y) = C - 2x - 2y$

Function may be a maximum or minimum for the solution of the simultaneous equations:

$C - 2x - y = 0$
$C - x - 2y = 0$

The solution is $x = C/3$ and $y = C/3$. For these values of x and y, $\frac{\partial^2 u}{\partial x^2}$ is negative and $\frac{\partial^2 u}{\partial x^2} \cdot \frac{\partial^2 u}{\partial y^2} - \frac{\partial^2 u}{\partial x \partial y}$ is greater than zero. Therefore the number C should be divided into three equal parts if the product of these parts is to be a maximum.

3. $\partial V/\partial a = k(b - x)$; $\partial^2 V/\partial a^2 = 0$
$\partial V/\partial b = k(a - x)$; $\partial^2 V/\partial b^2 = 0$
$\partial^2 V/(\partial a \partial b) = 0$

The given function has no maxima or minima.

4. $\partial M/\partial y = e^x \cos y$; $\partial N/\partial x = e^x \cos y$. The differential is exact and $u = e^x \sin y + C$.
$\partial M/\partial v = nV^{n-1}$; $\partial N/\partial p = nV^{n-1}$. The differential is exact and $u = pV^n + C$
$\partial M/\partial y = -ax + 2y$; $\partial N/\partial x = y - 2ax$. The differential is inexact.

5. $\frac{\partial M}{\partial y} = 2x$; $\frac{\partial N}{\partial x} = 2x$. The differential is exact and $u = x^2y$.

$$\int_{0,0}^{4,3} (2xydx + x^2dy) = x^2y \Big|_{0,0}^{4,3} = 48$$

As the next part of the problem appears in THE JOURNAL it is also exact and the value is independent of the path. If the problem had read $\int_{0,0}^{1,1} (ydx - xdy)$ the differential would have been inexact. In this case if $y = x^2$ is adopted as the equation of a path passing through the points 0,0 and 1,1, the integral reduces to $\int_0^1 - x^2dx = -1/3$. If $y = x^3$ is adopted as the path, the integral is $\int_0^1 - 2x^3dx = -1/2$.

6. U is a function of three variables, p, V, T, any two of which may be taken as the independent variables.

$$dU = (\partial U/\partial T)_V\, dT + (\partial U/\partial V)_T\, dV$$

This is substituted into the expression for dQ and we have:

$$dQ = (dU/\partial T)_V\, dT + [(\partial U/\partial V)_T + p]\, dV$$

Testing this for exactness we obtain: $\frac{\partial^2 U}{\partial V \partial T} \neq \frac{\partial^2 U}{\partial T \partial V} - \frac{\partial p}{\partial T}$.

dQ is an inexact differential.

$$dQ/T = (1/T)(\partial U/\partial T) + (1/T)[(\partial U/\partial V) + p]\, dV$$

Testing this for exactness we obtain:

$$\frac{1}{T}\left(\frac{\partial^2 U}{\partial V \partial T}\right) \overset{?}{=} \frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial V}\right) - \frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right) + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right) - \frac{p}{T^2}$$

Since order of differentiation is immaterial and since under the conditions of the problem $\partial U/\partial V = Q$, the above becomes:

$$(1/T)(\partial p/\partial T) = p/T^2$$

$$\partial p/\partial T = R/V$$

$$R/(VT) = p/T^2, \text{ or } pV = RT.$$

Therefore we have proved that for a perfect gas dQ is an inexact differential and dQ/T is an exact differential.

LABORATORY PREPARATION OF HYDROFLUORIC ACID

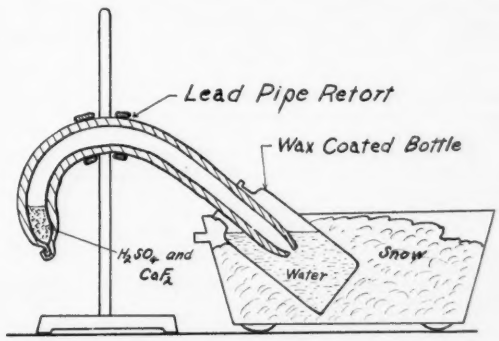
ARNOLD BOOKHEIM

Williamson Central School, Williamson, New York

LACKING a supply of hydrofluoric acid in our stock room, we found it necessary, in order to etch glass, to make hydrogen fluoride from calcium fluoride and sulfuric acid in a lead dish. Several members* of our chemistry class, in working out a project, found they had a considerable amount of etching to do. They decided to make some hydrofluoric acid.

The apparatus used (see diagram) consisted of a retort made of about two feet of $1^1/_4$" I.D. lead pipe. A lead bending spring was placed in the pipe and it was bent to the proper curve. The spring was removed by beating the sides of the curved pipe with a wooden paddle. The surplus on the ends was trimmed off and the discharge end was brought down to a smaller size by beating with the same paddle. No lead-burning outfit was available, so the reaction end of the retort was closed by flattening one inch of the pipe in a vise and folding over one half of the flattened portion.

Powdered calcium fluoride was placed in the retort by means of a long paper cone, and concentrated sulfuric acid was poured in through a funnel and rubber tube. The discharge end of the retort was placed inside a paraffin-coated bottle containing distilled water, and the bottle was surrounded by snow in a pneumatic trough. The retort was then heated for forty minutes.



LABORATORY PREPARATION OF HYDROFLUORIC ACID

The liquid was tested by allowing a microscope slide to stand in it overnight. The slide was half dissolved the next morning. The necessary etching was then done with this home-made hydrofluoric acid.

* DOUGLAS TASSEL, RALPH AMELEE, AND WORTH GETCHELL.

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F. B. Dains
Tenney L. Davis
J. Howard Graham
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J. W. Howard

ABSTRACTS

R. A. Baker, *Abstract Editor*

D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
E. D. Walter
E. Roger Washburn
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

Salt highways. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **105**, 4 (Oct., 1935).—Roadways of salt are being sponsored by the International Salt Co. and are constructed under a method discovered by Dr. Cloyd D. Looker, research director of the company, and developed in conjunction with Dr. H. Ries, professor of geology, Cornell University. About 100 miles of such salt highways have been laid in various parts of the country in cooperation with several other producers of rock salt, in New York, Michigan, Vermont, Ohio, Kansas, Maryland, Indiana, Louisiana, Mississippi, and Pennsylvania. After several months' use, they have proved satisfactory. The roads are built of clay and gravel treated with a compound made of the same kind of rock salt that goes into an ice-cream freezer. The rock salt, it is claimed, not only compacts the clay, giving it a concrete effect, but also crystallizes in the road surface and retards the evaporation of moisture, keeping the top moist and firm. When this takes place, the surface sheds water, providing a practically nonskid road. The mixture is intended for secondary roads and to provide firm surfacing at a small cost, as its cost per mile is about one-third that of asphalt and one-ninth that of cement necessary for a concrete road. G. O.

A contribution to the fluorescence of substances. J. Plotnikow. *Chem.-Ztg.*, **59**, 597 (July 20, 1935).—Out of 141 different flowers examined, 100 showed no fluorescence and 36 faint fluorescence. Relatively high fluorescence was obtained with turkey cress (bluish white), wild mallow (violet), forget-me-not (white and yellow), and orchis (green). Many drugs were found to fluoresce strongly, as *e. g.*, wormwood (yellow), Asiatic poppy-seed (blue), and meadow saffron (blue). Among the mushrooms *rosa agaric* yields a reddish fluorescence. The resins give certain colors in the solid state and others in solution depending upon the solvent. Among the organic compounds tested palmitic acid gave a greenish blue, stearic acid a violet, and benzotrichloride a bluish white fluorescence. Only 20 out of 140 dyes exhibited this phenomenon. Out of 90 minerals tested most of them gave the known effect while others did not do so; thus calcite from Vrapče near Zagreb showed up white instead of pink. The water lily gave positive results (deep green) as did beetles (eyes mostly), toads (abdomen bluish white, the back hardly at all, the eyes greenish yellow). L. S.

Which lime for what use? S. P. Armsby. *Chem. Industries*, **37**, 437–40 (Nov., 1935).—Lime has been employed as an industrial chemical reagent since the dawn of civilization, and is today one of the most widely used of the chemical raw materials. Yet, in spite of the wide diversity of its uses and its vital importance to a host of our modern process industries, its efficient utilization is seriously handicapped by a surprising lack of information regarding its fundamental chemical and physical properties. Many important chemical manufacturing industries, using large quantities of lime, fail to secure from it the service they should for one or more of the following reasons:

1. Lack of coördination between the process requirements of the customer and the manufacturing methods employed by the lime producer.
2. Failure to appreciate the variations in characteristics of limes from different sources.
3. Faulty purchase specifications, resulting from misunderstanding of the properties of lime and of their effects upon process operations.
4. Improper use of lime, because of incorrect classification of its properties or because of failure to understand certain definite effects introduced by certain specific properties or impurities.

A. T. B.

Benzyl cellulose. R. C. Bickmore. *Chem. Industries*, **37**, 445–7 (Nov., 1935).—Formerly the high cost of etherifying agents necessary for the production of cellulose ethers (methyl, ethyl, glycol, and benzyl celluloses) has made the latter compounds relatively expensive as compared with nitrocellulose, cellulose acetate, etc. Nevertheless, their general satisfactory properties, including stability, freedom from discoloration of films, coatings, etc., on exposure to ultra-violet light, solubility in many common solvents, relative non-inflammability and sometimes low hygroscopicity, have drawn attention to their possible technical applications.

It would appear that benzyl cellulose has possibilities as the basis of lacquers, enamels, and various coating compositions and dopes; linoleum substitutes, celluloid, safety-glass fillings and thermoplastic molding materials and masses; insulating compositions, silk, airplane dopes, and artificial leather.

The manufacture of benzyl cellulose is rather complicated, although entailing few direct stages, on account of the number and undesirable nature of the by-products formed. A. T. B.

Electrotypers' waxes. C. F. Mason. *Chem. Industries*, **37**, 443–4 (Nov., 1935).—After suggesting the possible reason for the individual ingredients of a typical electrotypers' wax, Mr. Mason tells us that electrotyping is an industry which is based upon scientific principles which are being investigated in our universities, government bureaus, and industrial laboratories, but that apparently all useful knowledge has been applied in an electrical and mechanical sense, and that the wax side has been more or less of an art. "The waxes are ready for changes because the science has nearly overtaken it." A. T. B.

Hydrosulfite processes and their preparation. *Chem. Industries*, **37**, 449–51 (Nov., 1935).—Although there is copious literature concerning hydrosulfite, information of a practical order is sparse and scattered, and there are gaps that detract from its value. This article attempts to organize available bits of information concerning hydrosulfite. A. T. B.

Chem. & Met.'s new process and flow sheets. Anon. *Chem. & Met. Eng.*, **42**, 595–610 (Nov., 1935).—Flow sheets are given for the following industries: Titanium Dioxide Pigment; Polymer Gasoline; Vinyl Acetate; Direct Acetic Acid; Gasoline Treatment; Electrothermic Zinc Oxide; Fink Aluminum Coating Process; Bromine from Sea Water; Petroleum Distillate Deasphaltization; Continuous Saponification; Cement Rock Beneficiation; Sewage Disposal; Caustic Soda Recovery in Viscose Manufacture; Gas Purification; Phosphate Rock Beneficiation; New Sugar Processes; Continuous Fatty Acid Refining; Superphosphate, Anode Process of Rubber Deposition; Iodine from Oil Brines; Lactic Acid from Whey; Fermentation CO_2 Purification; Paper De-inking; Black Liquor Recovery; SO_3 from Waste $FeSO_4$. J. W. H.

What research creates, chemical engineering achieves. S. D. Kirkpatrick. *Chem. & Met. Eng.*, **42**, 588–94 (Nov., 1935).—This year the award of Chemical & Metallurgical Engineering went to the Organic Chemical Department of E. I. du Pont de Nemours & Co. Their outstanding achievement of the past two years is the successful industrial development of synthetic rubber (Duprene), synthetic camphor, and other important chemicals and dyestuffs. Synthetic rubber is made from acetylene. It has better oil and heat resistance than natural rubber. It does not check and crack so readily. The synthetic camphor is made from American turpentine. It is a highly refined product and is rapidly replacing natural camphor in the manufacture of pyroxylin plastics, films, and safety glass. J. W. H.

Building gasoline. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **106**, 1–2 (Nov., 1935).—Practical methods of increasing the yield of useful products of petroleum are becoming more and more important. One method has reached significant commercial importance and development; that is, polymerization into gasoline of the gases from petroleum-cracking operations, which are

now used mostly as fuels. Interest in this method is increasing since the resulting gasoline has not only anti-knock properties but also a blending value higher than the octane number would indicate. Polymerization may be looked upon as the opposite of cracking as applied to the formation of gasoline. In the cracking processes the heavy, high-boiling portions are broken down to form low-boiling, light liquids. In polymerization the very light gaseous products are built up to form these low-boiling liquids. There are three types of polymerization processes now available, differing principally in temperatures, pressures, and use of catalysts. Based on a conservative estimate of 3.5 gallons of gasoline from 1000 cubic feet of cracked gas, there is a possibility of producing over a billion gallons of gasoline from the 300 billion cubic feet per year of such gas, all of which will have its effect on costs and conservation. Special fuels, such as those for aviation use, form the most important outlet for the polymerized gasoline. An important potential field for these polymerization processes lies in the conversion of cracked gases into aromatic hydrocarbons which constitute the raw materials of important divisions of industrial organic synthesis, including dyestuffs, pharmaceuticals, and perfumes. G. O.

Rolling metals. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **106,** 3 (Nov., 1935).—The direct rolling of metals is one of the recent developments in the metal industries that is of serious interest. The idea is not new. Bessemer himself realized its possibility and actually tried it in 1846. A patent was issued as early as 1865, but Bessemer was unable to realize completely the possibilities that seemed promising to him. This process, now in small commercial production on brass and well under way for several metals, including steel, will mean, it is believed, cheaper steel with less capital investment. In principle the process is simple. Molten metal is poured between rolls spaced so closely as to approximate the sheet thickness desired. Chilling occurs at the same time with the rolling operation. With steel two major difficulties are being faced—crystal structure and surface characteristics. G. O.

Back to the soil. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **106,** 3–4 (Nov., 1935).—Farmers are again using increased amounts of fertilizers supplied more than ever by American chemicals. Nitrogen, potassium, and phosphorus are still the three main plant foods. Of these phosphorus has been by far the most important to the fertilizer trade. Potash, for decades a German-Alsatian monopoly, is now a competitive article. American, Spanish, Russian, and Palestinian (Dead Sea) production is responsible. The U. S. supplies about half of its potash requirements, chiefly from the deposits of New Mexico. Inorganic nitrogen was a Chilean monopoly or a by-product from coke manufacture. Nitrogen fixation has altered this situation, and nitrogen-fixation plants have been set up in every country of any military importance. Improvement of mixed fertilizers continues. Ammoniation of superphosphates has made rapid progress. The next major advance in fertilizer utilization is likely to relate to acidity control of the soil. Such acidity may be corrected by the addition of limestone or dolomite to the soil or by substituting these materials for a part of the inert fillers added to fertilizers. Manganese, sulfur, iron, and copper are likewise proving important especially in the Everglades. A new market for fertilizers may arise for protection against soil erosion. G. O.

Using the bark. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **106,** 4 (Nov., 1935).—Bark, a nuisance by-product of timber industries, is now being put to use as Permex, a new flooring material. Permex is composed of ground bark and inert mineral fillers. The material is said to resist abrasion, not to absorb oils or stain readily, not to become sticky or rough, and not to scar. Factory floors, especially trucking aisles, elevator approaches, and shipping platforms, are the first sales approach; but it is even recommended for specialties, such as desk, table, and counter tops, and for electrical paneling. G. O.

Billingham hydrogenation plant. ANON. *Nature*, **136,** 635 (Oct. 19, 1935).—On October 15th occurred the formal opening of the coal hydrogenation petrol (gasoline) plant of Imperial Chemical Industries, Ltd., at Billingham-on-Tees. This British plant is the first in the world to make petrol on a commercial scale from bituminous coal. It was originally intended to produce 100,000 tons a year of petrol from coal, but it was later decided to increase capacity to 150,000 tons, the extra amount to be made either from coal or creosote oil and low-temperature tar. The general procedure is as follows: the raw coal is cleaned to less than $2^1/_2$ per cent of ash and is ground up with oil previously made in the process to make a 50 per cent. coal-in-oil paste. This is hydrogenated at 250 atmospheres and 450°C. The crude oil is distilled into heavy oil, middle oil, and petrol; and the heavy oil and middle oil further hydrogenated to increase the yield of petrol. The whole of the coal is transformed into a small, solid, consumable residue, gas and petrol. The coal consumption is estimated as 4 tons of coal to 1 ton of petrol produced, and 40,000 tons of petrol have already been made. It involves a huge investment, but gives a certain amount of independence to countries without oil reserves. F. B. D.

The regeneration of lubricating oils. See this title under Scientific Reviews and Bibliographies; Tabulations of Scientific Data.

Non-breakable glass. See this title under Scientific Reviews and Bibliographies; Tabulations of Scientific Data.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

The preparation of artificial resins as a school experiment. H. LINDNER. *Z. phys. chem. Unterricht.*, **48,** 251 (Sept.-Oct., 1935).—The artificial resin known as Edelbakelit in German industry is formed by condensation of phenol and formaldehyde with the exclusion of water. The product can be obtained in the following school experiment. Heat 50 g. of crystallized white phenol, 100 cc. of 35% formaldehyde, and 5 cc. of 30–40% KOH in a beaker under the hood to a temperature of 107° until test drops removed from time to time assume a honey-like consistency, when the heating is interrupted. Pour the contents into a dish or a glass tube, close with a cork stopper, and let harden for several hours at 60–65°C. An inexpensive oven can be constructed from a tall tin can covered with a flower pot and provided with a thermometer through the center. The heat is produced with a 25-watt light bulb. The dish with the material is placed on a wire frame over the light bulb. The temperature should not exceed 70° (to avoid foaming). The hardening operation is completed after 3–4 hours, yielding a ruby-red solid product. L. S.

A simplified Victor Meyer apparatus. H. C. PALMER. *Sch. Sci. Rev.*, **16,** 559 (June, 1935).—An apparatus made from materials at hand in the laboratory is described. S. W.

A dilatometric law of mass action experiment. E. J. LEEMING. *Sch. Sci. Rev.*, **16,** 560 (June, 1935).—The rate of hydrolysis of acetal may be measured by following the increase in volume of the solution. The elimination of the usual large number of titrations renders this experiment especially suitable as a laboratory exercise. A simple graduated dilatometer for this purpose is described. S. W.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES; TABULATIONS OF SCIENTIFIC DATA

Photochemistry. F. BRIERS. *Sch. Sci. Rev.*, **16,** 458–69 (June, 1935).—An elementary discussion of the common photochemical reactions. S. W.

Recent work in inorganic chemistry. A. J. MEE. *Sch. Sci. Rev.*, **16,** 470–9 (June, 1935).—A review covering the years 1933–34. 38 references. S. W.

The chemistry of the vitamins—I. K. H. COWARD. *Sch. Sci. Rev.*, **16,** 514–22 (June, 1935).—A brief review of vitamins A, B_1, B_2, B_3, and B_4 (G). 16 references. S. W.

Biochemistry and the medical importance of the newer pyridine derivatives. A. BINZ. *Angew. Chem.*, **27,** 425–9 (July 13, 1935).—A review. 46 references. L. S.

The chemistry of saponins. R. TSCHESCHE. *Angew. Chem.*, **48,** 569–73 (Aug. 31, 1935).—A review. L. S.

The regeneration of lubricating oils. E. BOSSING. *Chem.-Ztg.*, **59,** 557–9 (July 10, 1935).—A review. 54 patents are discussed. L. S.

Non-breakable glass. E. BOYE. *Chem.-Ztg.*, **59,** 582–4 (July 17, 1935).—A review of 64 patents. L. S.

The discovery of neutrons, positrons, and artificially produced radioactivity. E. THILO. *Z. phys. chem. Unterricht*, **48,** 170–9 (July-Aug., 1935).—A lecture reviewing the historical development. 30 references. L. S.

HISTORICAL AND BIOGRAPHICAL

Adolf von Baeyer—1835–1917. J. R. PARTINGTON. *Nature*, **136**, 669–70 (Oct. 26, 1935).—Two of the outstanding organic chemists of the later nineteenth and early twentieth centuries were Adolf von Baeyer and his pupil, Emil Fischer. As the late W. H. Perkin said, "Their influence has been profound, mainly, no doubt, because of the great amount of work which they have left behind, but to a scarcely less degree by reason of their influence as teachers."

Baeyer, who was born October 31, 1835, was a student of Bunsen and Kekulé. His teaching life was spent in a small technical school in Berlin, at Strassburg (1870–75), and at Munich, where he succeeded Liebig. (The teaching life of Liebig and Baeyer spanned nearly a century.)

His work covered many fields: for instance, uric acid; condensation reactions with acetone, and with hydrocarbons and phenols, and phthalic anhydride which led to the discovery of the phthaleins, fluorescein, etc.; fundamental work on indigo; phloroglucinol; organic peroxides and oxonium compounds. His strain theory is in all textbooks. With his death in 1917 passed one of the great builders of organic chemistry.

F. B. D.

Martin Dennis—chief chemist to the tanners. ANON. *Chem. Industries*, **37**, 429–33 (Nov., 1935).—His heart set upon becoming a surgeon, Martin Dennis suddenly, in the depression period following the panic of 1873, found himself forced to enter into the hurly-burly of business. Nevertheless, he quickly accepted an offer made to him by his uncles, David McAlpin and George Rose, to superintend their plant at Yonkers, New York, producing a wide range of commercial leathers of many weights and finishes. He was one of the first to provide a logical basis for changing the ancient habit of rule-of-thumb tanning for he was one of the first to provide a basis of chemical logic for his innovations. He received a patent for his "one-bath" chrome tannage but even his uncles could see no profit in pioneering in such a well-rooted industry. He resigned, therefore, to go it alone. Such was his faith in his new discovery, but the job was not an easy one. Lack of working capital forced him to close down. So deeply did he believe that chrome leather was to make its place in the tanning industry that he decided to attempt the manufacture and sale of a chrome tanning compound. Together with Dr. H. E. Richards, his friend of college days, he formed The Martin Dennis Chrome Tannage Co. in 1893 to produce "Tanolin." After seven years of continual demonstrating some headway was made with a few tanners. The public immediately recognized the merits of the new leather and a demand for it grew steadily. Next Martin Dennis developed a chemical puer for hides and skins to replace the disgusting and unreliable natural manure bates used from ancient times. Then he introduced the use of oils in emulsified form to lubricate the tanned leather. From very small beginnings the business has grown until its products are to be found in use by tanners in all parts of the world.

A. T. B.

Bicentenary of James Keir, F.R.S., 1735–1820. ANON. *Nature*, **136**, 506–7 (Sept. 28, 1935).—James Keir was an able chemist and the friend of Erasmus Darwin, Boulton, Watt, Priestley, and Davy. Educated at the University of Edinburgh, he first entered the Army. Resigning his commission in 1768, he settled in the Midlands and devoted himself to geology and chemistry. He was, in turn, a glass manufacturer, assistant to Boulton and Watt at Soho, and founder of a soap and alkali works.

In 1776, he translated Macguer's "Dictionary of Chemistry," and in 1777 published a treatise on "Elastic fluids or gases." He also contributed chemical papers to the Royal Society. In 1789, he issued the first part of a chemical dictionary of his own, which was discontinued when he became convinced of the weakness of the phlogiston theory.

F. B. D.

Tercentenary of Robert Hooke (1635–1703). ANON. *Nature*, **136**, 56–7 (July 13, 1935).—**Robert Hooke and his contemporaries.** E. N. DA C. ANDRADE. *Nature*, **136**, 358–61 (Sept. 7, 1935).—"Of all the scientific worthies of the 17th century, none will be remembered longer than Hooke whose views and activities influenced the progress of scientific thought and practical physics to an incalculable degree."

During his student days at Oxford, he gained the friendship of the men who inaugurated the Royal Society—among them especially Boyle, whose experimental work owed much, at this time and later, to Hooke. In 1662, he was made curator of experiments to the Society. Later he was appointed to the chair of geometry in Gresham College, and to a lectureship founded in 1664 by Sir John Cutler. This gave him a position at thirty years of age somewhat resembling that of Faraday 150 years later.

"Hooke was a chemist, a physicist, an astronomer, an inventor, a mechanician, and an architect.

"To horologists he is known for his application of the balance-spring and the invention of the anchor escapement; by engineers he is remembered by his universal joint and his views on elasticity; as an instrument maker, he made improvements in thermometers, barometers, air pumps, and microscopes; he devised sounding apparatus for sailors.

"He was the first to describe the cellular structure of plants and the first to suggest the use that might be made of fossils in revealing the history of the earth. He had advanced views on gravity, colors, light, respiration, combustion, and the nature of heat." As an architect, after the great fire, he gained modest wealth from the buildings he designed.

During his life he suffered from ill health, and in his latter days, was probably a "lonely old bachelor." His diary, covering the years 1672–80, has just been published. It shows that during these years he mixed freely with his fellows, and the list of coffee-houses and taverns where he ate, smoked, and drank, number some one hundred and fifty. Among them is the Cheshire Cheese, so often visited by American tourists.

The diary is that of a man whose interests were concentrated on pure and applied science, and hence is very different from that of his friend, Pepys, "who was a gossip and a man about town."

Its notations indicate that he was especially intimate with Boyle and Sir Christopher Wren (he mentions the giving of a hobby horse to Wren's little son). It is also an intimate picture of the years 1672–80 and of the early history of the Royal Society—and its publication is an event in the history of science.

F. B. D.

Josef Tillmans. A. BÖMER AND A. JUCKENACK. *Z. Untersuch. Lebensm.*, **69**, 209–11 (Mar., 1935).—An obituary with portrait as frontispiece.

Josef Tillmans, professor of nutrition chemistry and director of the University Institute for Nutrition Chemistry in Frankfurt, Germany, died on Feb. 2, 1935 at Buchschlag near Frankfurt. He was born at Ramsdorf, July 4, 1876. He was an authority in the fields of water chemistry, sewage disposal, and food chemistry. He was author of the following texts: *Lehrbuch der Lebensmittelchemie* (1927); *Wasserreinigung und Abwasserbeseitigung* (1912); *Die chemische Untersuchung von Wasser und Abwasser* (1915, 1932). He wrote many papers dealing with vitamin C, especially its properties and its estimation in foods. Tillmans was skilful in applying the science of physical chemistry to food chemistry. Since 1930 he was co-editor of the journal in which this obituary appears, and since 1933 he was co-editor of *Handbuches der Lebensmittelchemie*.

E. D. W.

Our first great chemical enterpriser. ANON. *Chem. Industries*, **37**, 325–30 (1935).—George T. Lewis was no chemist, yet with the devotion of a true scientist he spent his life in solving the economic problems of chemistry. He turned his back on tempting opportunities to play an important and personally profitable rôle in the steel, coal, and petroleum industries, not because he was blind to those opportunities, but because he held fixed before him his vision of chemical opportunity. Born into a family of merchants, ship owners, and manufacturers, he started in 1834 at the age of sixteen at the bottom rung, as a clerk in the accounting department of the white lead factory of which his father was junior partner.

In 1856 the firm of John T. Lewis & Brothers was organized and with characteristic self-effacement, George T. Lewis placed his brothers in active control while he himself continued, as commission merchant under his own name, to sell the products of the Lewis lead factory. This connection was the basis of other similar arrangements and was the true bond between him and a number of chemical enterprises. While in close touch with the manufacture of white lead, he proved himself one of our first chemical conservationists by working out a successful method for the recovery of lead in the smelter fumes that had formerly gone to waste. As was his custom, in attacking this problem he associated with himself a good technical man. Because he built anew a failing alkaline salt business he earned the title of "Father of the Salt Company." It was preëminently a characteristic of George T. Lewis' business methods that he furnished the ideas and then called upon others to work out the details and to carry them forward to successful execution.

A. T. B.

The discovery of neutrons, positrons, and artificially produced radioactivity. See this title under Scientific Reviews and Bibliographies; Tabulations of Scientific Data.

RECENT BOOKS

ANALYTICAL CHEMISTRY, VOLUME II, QUANTITATIVE ANALYSIS. Based on the text of *F. P. Treadwell*, late of the Polytechnic Institute of Zurich; translated, enlarged, and revised by *William T. Hall*, Massachusetts Institute of Technology. Eighth edition. John Wiley & Sons, Inc., New York City, 1935. xiii + 858 pp. 152 figs. 15 × 23 cm. $6.00 net.

For many years the Treadwell-Hall Quantitative Analysis has been recognized as a standard reference book on methods of quantitative analysis. In the new edition, the material has been revised completely and many older analytical methods have been discarded in favor of newer and better ones; but the main outline of the book remains unchanged.

An Introduction comprising the first 54 pages contains a description of weights and weighing, filtration, sampling, and other general analytical processes. This is copiously illustrated and provides a wealth of practical details of laboratory technic.

Part I contains 245 pages devoted to the gravimetric determination of the metals, grouped according to their chemical properties. Several methods are usually given for the separation of the element under consideration from others most like it, and its final determination. The last 160 pages of this section are devoted to the gravimetric determination of non-metallic elements and radicals. In addition to the analysis of inorganic substances, a number of organic methods are taken up. These include combustion for carbon and hydrogen, the Carius method for halogens, and Dumas' method for nitrogen.

Part II contains 218 pages devoted to volumetric analysis. A description of the standardization and use of volumetric apparatus is followed by a brief discussion of neutralization indicators and the methods of acidimetry and alkalimetry to which they are suited. The next subject, comprising half of this section, deals with the theory of oxidation and reduction in solution and the processes based upon these reactions. The last section deals with precipitation titrations.

Part III consists of 80 pages devoted to Gas Analysis. In addition to the analysis of illuminating gas and other hydrocarbon mixtures, the analysis of inorganic gases like chlorine and sulfur dioxide is taken up.

The next 40 pages contain a large collection of conversion tables and tables giving the densities of solutions and the properties of compounds useful in analytical procedures. The last 50 pages of the book are taken up with a very complete author index and subject index. The volume is clearly printed in good type on good paper; well illustrated and attractively bound.

This book can be recommended as an excellent reference work for the advanced analytical student, teacher, or research worker who wishes specific information on analytical processes. It contains useful experimental details and references to the original literature. It does not attempt to give the theoretical background of the analytical processes which would be necessary in an elementary text, although it might well serve as supplementary reading on laboratory technic for the elementary student, or furnish a choice of laboratory experiments for such a course.

FRANK T. GUCKER, JR.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

PRINCIPLES AND APPLICATIONS OF ELECTROCHEMISTRY. VOL. II. APPLICATIONS. *W. A. Koehler*, West Virginia University. John Wiley & Sons, Inc., New York City, 1935. xiv + 545 pp. 245 figs. 15 × 23 cm. $5.00 net.

This book is the companion to "Vol. I, Principles, " by H. J. Creighton, and a worthy companion it is. The attempt has been made to develop a textbook for students and a reference work for industrial electrochemists. Based on ten years' experience in teaching the subject, it is a very fine text. With the coöperation of numerous specialists it does not come far short of realizing the second goal. It is amazing how much first-class material Dr. Koehler has succeeded in compressing into one moderate-sized volume.

The chapter on the economics of power generation, though short, is very good. The review of theoretical electrochemistry could have been omitted, in view of Creighton's work, or at least condensed to a few essential definitions, formulas, and concepts. If this book were intended to be self-contained, it could well be rearranged and expanded to include more of the principles utilized later. Primary cells and especially secondary cells are handled very well. A fuller discussion of fuel cells, although at present of theoretical interest only, might well be included. Electroplating, electroplating solutions, and electrorefining are discussed with unusual detail. The same may be said of electrometallurgy, both of aqueous solutions and fused salts. The discussion of the electrolysis of alkali halides is satisfactory. A little more on the theoretical principles involved might help.

The chapters on electrolytic oxidation and reduction and on oxygen and hydrogen production are very good. A brief, though satisfactory discussion of corrosion is included. Unusual in such works is the chapter on electroanalysis. The chapters on electric furnaces and their uses in the metallurgical and nonmetallurgical industries are noteworthy. Electronics are treated much more fully than is common and this is quite desirable. The chapters on ozone production and nitrogen fixation are satisfactory. Separation by electrical means is very fully discussed. The chapter on miscellaneous electrochemical processes is something new and well worth including.

The book includes 35 tables of useful data and an abundance of references. Operating details are very full. The illustrations are excellent. Both subject and author indexes enhance the value of the work. Type, format, and style of the author combine to produce a most attractive book.

In conclusion the reviewer desires to compliment the author and publisher and to recommend this book without reservation. It is realized that space considerations forbid the inclusion of certain material mentioned above, so no adverse criticism is intended. Electrochemical workers will need this work and every teacher of the subject should consider carefully its use as a text

MALCOLM M. HARING

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A TEXTBOOK OF ORGANIC CHEMISTRY, Historical, Structural, and Economic. *John Read*, University of St. Andrews. Second edition. G. Bell & Sons, Ltd., London, 1935. xiv + 703 pp. 87 figs. 12.5 × 19 cm. Price 12/6 (approx. $3.10).

The first edition of this textbook was published in 1926, and the author has thoroughly revised it in order to bring it up to date. This text places especial emphasis on (*a*) the historical development of organic chemistry; (*b*) the deduction of structural formulas; and (*c*) the correlation of academic, technical, and economic phases of organic chemistry.

Part I of the book is devoted to the "Historical Development" of chemistry. While much of this material does not deal with organic chemistry, the author justifies its inclusion by pointing out the fact that the student in general chemistry is not interested in the historical aspect until after he has acquired some knowledge of the fundamental principles of chemistry. However, by the time the student begins his study of organic chemistry he is able to appreciate the difficulties encountered in the elucidation of the laws of chemistry, the rise of the atomic theory, and the development of structural formulas. The sixty pages devoted to this historical phase constitute an excellent summary of the important events in the development of chemical theory.

The second part of the text is entitled "Molecular Diagnosis." A clear, readable discussion of the methods of purification, elementary analysis, and the determination of empirical and molecular formulas is given.

Aliphatic or open-chain compounds are considered in Part III, and cyclic or closed-chain compounds in Part IV. The discussion of each homologous series is characterized by the fact that the author has chosen to deal very extensively with a few typical compounds from each series. The historical aspect is also emphasized in these two parts by the introduction of special paragraphs discussing the important events in the production of the compounds and their structural proofs. Structural formulas are discussed in some detail and emphasis placed on the reasons for assigning certain atomic arrangements in the molecule.

This revised edition contains accounts of some of the newer methods for the preparation of organic compounds. The author also indicates the price (in shillings) of various substances in order to give the student some idea of the relative value of organic compounds. Brief chapters on hormones, vitamins, and electronic theory have been added.

The technical methods cited for producing organic compounds and the discussion of the economics of their production are probably more applicable to conditions in Great Britain, with which the author is familiar. It is evident that the important industrial methods vary in different countries because of differences in raw materials, sources of power, etc. Hence, the book does not treat adequately many of the important industrial processes in use at the present time in the United States. For example, the author mentions that ethyl alcohol may be produced from acetaldehyde or from ethylene, but states on p. 182 that it is unlikely that these substances will displace starch and sugars as the main source of alcohol. Several pages are devoted to the wood distillation industry, and only one short paragraph to the carbon monoxide-hydrogen reaction for the production of methanol. No mention is made of the fact that this reaction is used to obtain certain of the higher alcohols. The production of acetone by dehydrogenation of isopropyl alcohol, the many synthetic organic chemicals obtainable from ethylene and the production of synthetic rubber-like products, such as duprene, are not discussed.

The book is written in an interesting historical yet logical style. It is well printed and remarkably free from errors. One mistake which was noticed was the statement (p. 148) that only four of the five isomeric amylenes are known.

Occasionally, certain terms are used rather loosely. For example, the term polymerization is used in the old historical sense, and not in agreement with modern ideas of this type of a reaction. It is used to describe the conversion of acetylene to benzene and acetaldehyde to ethyl acetate, but is not used in discussing the relationship of monosaccharides to polysaccharides. The latter are said to be formed (p. 409) "by a process of repeated anhydride-formation." No mention is made of the fact that the cyclic sugar structures are hemi-acetals, and that di- and polysaccharides are acetals.

The book is designed for a year's course in organic chemistry, and is one of the best textbooks of the English school.

R. L. SHRINER

DEPARTMENT OF CHEMISTRY
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EXERCISES IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. *Horace G. Deming*, Professor of Chemistry, University of Nebraska, and *Saul B. Arenson*, Associate Professor of Inorganic Chemistry, University of Cincinnati. Fourth edition. John Wiley & Sons, Inc., New York City, 1935. xv + 326 pp. 25 figs. 13.5 × 21.5 cm. $1.80.

This manual was first published in 1924. The order of topics is very nearly that of the fourth edition of Deming's "General Chemistry." As stated in the preface, "New experiments have been added on photography and the sensitivity of qualitative tests, and many of the remaining experiments have been improved as the result of experience with our students, or following the suggestions of other teachers." The chief aims of an elementary course, according to the authors, are: (1) to make the student familiar with a few representative types of matter; (2) to reveal some of the general principles that govern the transformation of matter; (3) to afford some experience with experimental methods.

There are 75 exercises in the manual, which cover 226 pages. A wide range of experiments is offered. In general, the directions and comments are clearly written and are accurate and adequate. The directions for weighing, however, are inadequate for students doing quantitative experiments.

Here and there the manual departs from the order of Deming's "General Chemistry." Thus, the derivation of chemical formulas is taken up in Exercise 17, p. 55; but in the textbook it is postponed to Chap. XXXVI, p. 569.

In the manual the good old term "hydrogen-ion," H^+, is still used (p. 97), while in the textbook "oxonium-ion" is used quite consistently (pp. 194 and 520).

The second part of the book is devoted to qualitative analysis. Since the exercises fill 226 pages, the space left for qualitative analysis is reduced to less than 100 pages. The instructions and outlines are clear and to the point, but the theoretical matter is limited. Instructions are given for the separation and identification of the cations, for preparing solids for analysis, and for testing for the common anions. The reviewer would like to call attention to one error, namely, the statement that arsenic acid in solution is slowly reduced by H_2S to arsenious acid (pp. 249–50): $H_3AsO_4 + H_2S \longrightarrow H_3AsO_3 + H_2O + S$. This is the old hypothesis of Rose, which was disproved by L. W. McCay nearly a half century ago. [MCCAY, *Am. Chem. J.*, **10**, 459 (1888).] He has shown that arsenic acid is never reduced by H_2S directly to arsenious acid and free sulfur. His experiments have proved that *monosulfoxyarsenic acid* (H_3AsO_3S) is first formed, which loses sulfur, and then interacts with more H_2S to form As_2S_3. These changes may be formulated thus:

$$(1)\quad H_3AsO_4 + H_2S \longrightarrow H_3AsO_3S + H_2O,$$
$$(2)\quad H_3AsO_3S \longrightarrow H_3AsO_3 + S,$$
$$(3)\quad 2H_3AsO_3 + 3H_2S \longrightarrow As_2S_3 + 6H_2O.$$

McCay's results have been confirmed by the reviewer. [FOSTER, *J. Am. Chem. Soc.*, **38**, 52 (1916).] The Rose hypothesis is in many modern books on chemistry, which shows how difficult it is to eradicate error.

"Exercises in General Chemistry" as a whole lays a solid foundation for further work in chemistry. The book is well printed and bound, and is in every way a suitable companion volume for Deming's "General Chemistry."

WILLIAM FOSTER

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ORIGINS AND DEVELOPMENT OF APPLIED CHEMISTRY. *J. R. Partington*, M.B.E., D.Sc., Professor of Chemistry in the University of London, Queen Mary College. Longmans, Green and Co., London, New York, Toronto, 1935. xii + 597 pp. 15.5 × 24.8 cm. 45 shillings net ($16.50 in U. S. A.).

This is a book of a new kind, a history of pre-chemistry, a history of the chemical practices of the ancients which are deducible from the findings of archæology. It is much more than an account of the origins and early development of applied chemistry. Dealing primarily with the materials which the ancients used for all purposes, what they were, how they were used, where they were procured, etc., it inevitably makes mention of the trade relations, wars, voyages, etc., which often determined the spread of knowledge about them. It is therefore a history of the archæological period, from 4000 or 3000 B.C. to about the beginning of the Christian era, a history of culture in the sense that it supplies an account of what the ancient peoples were doing.

The book is divided into sections which deal respectively with Egypt, Babylonia, and Assyria, the Ægean Civilization, Troy and Cyprus, Asia Minor, Persia, Phœnicia, and Palestine. Professor Partington says that he had at first intended to include sections on India and China but abandoned the intention "after much material had been collected, partly because these regions in some way lie apart from the rest of the world in their

technical processes, but more particularly because the information at present available seemed insufficient as compared with that for the other regions." Each section is subdivided into portions which treat first of the chronology and general history of the civilization, then of its materials. All significant facts about the materials appear to be reported, chemical analyses and other studies which have been made upon them, and the conclusions which have been reached concerning their preparation and use.

The following incomplete list of the subdivision headings in the section which deals with Egypt gives an indication of the contents of the book, the other sections, subject always to the availability of material, being subdivided in a similar manner.—The Metals in Egypt, Temple Workshops and Libraries, Labour and Crafts, The Production and Uses of Fire, Fuel, Blowpipe and Bellows, Gold, Predynastic and Early Gold, Composition of Egyptian Gold, Stocks of Gold, Asem, Composition of Electrum, Silver, Chesbet, Mafek, Gems, Copper, The Discovery of Copper, Egyptian Mining in the Sinai Peninsula, African Copper, Hardening of Copper, Bronze, Tinned Copper, Sources of Egyptian Tin, Lead, Brass and Zinc, Antimony, Mercury, Platinum Metals, Iron, The Names and Representations of Iron, Sources of Iron, Predynastic Iron in Egypt, Egyptian Specimens of Iron, Steel, Stone, Plaster and Stucco, Bricks, Pottery, Black-Topped Pottery, Glaze and Glazed Ware, Colours of Glaze, Glass, Gilt Glass, Colourless Glass, Blowing Glass, Analyses of Egyptian Glasses, Imitation Gems, Vasa Murrina, Enamels, Pigments, Media, Encaustic Painting, Eye Paint, Salt, Natron, Sal Ammoniac, Alum, Sulphur, Nitre, Textiles, Dyes and Dyeing, Pomade and Ointment, Oils, Manna, Incense and Perfumes, Frankincense and Myrrh, Kyphi, The Mummy, Materials Used in Embalming, Egyptian Medicine, Physicians and Priests, Imhotep, Magic in Medicine, Medical Texts, Woods, Drinks, Beer, Vinegar, Wine, Bread, Leather, Detergents, Ivory, Various Animal Products, Writing Materials, Ink.

Partington's book is a work of the first magnitude, one that may some day perhaps be revised or enlarged but one that need never be rewritten. It will be indispensable to the student of the history of chemistry and to the student of the history of science and culture. The archæologist will wish to take a copy of it with him to the site of his excavations. The great museums of the world will not wish to get along without it. The student of economics will be interested in the weight and relative value of the ancient coins, in the gold-silver ratio among the various nations at various times, in the effect of Alexander's conquests upon it, and in the two dark ages of ancient Egypt concerning one of which a text says that "irrigation was neglected, trade was at a standstill, and cedar wood, grain, gold and charcoal were lacking." The teacher of chemistry will find in the book much material for use in his classes—for example, the hard copper of the Egyptians produced by "under-poling" and deriving its hardness from the cuprous oxide which it contained, or the use of alum for the fireproofing of wooden construction. The casual browser in the book will find in it much to stimulate his imagination.

The print job is difficult but well done, and the price of the book, though high, is by no means incommensurate with its value.

TENNEY L. DAVIS

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LABORATORY AND WORKBOOK UNITS IN CHEMISTRY. *Morris W. Ames*, Chairman of the Department of Physical Sciences, George Washington High School, New York City, and *Bernard Jaffe*, Chairman of the Department of Physical Sciences, Bushwick High School, New York City. Silver, Burdett and Co., New York City, 1935. Thirty-seven figures, seven important tables, one page of first-aid advice, and one page of cuts identifying 22 pieces of chemical apparatus. In two forms. The consumable form is paper bound, xii + 228 pp. 15 × 26 cm. List price, $0.84. The non-consumable form is cloth bound, xiv + 240 pp. 14 × 20 cm. List price $1.08.

This book of fifty-one well-organized units is intended to provide laboratory work and study exercises for the student, and demonstrations for the teacher throughout the beginning year of high-school chemistry. It is stated that the selection of materials is based on the suggestions and requirements of state and college entrance syllabi, on textbooks and the long experience of the authors as teachers of high-school chemistry. While the book may be used with any high-school text, the order of the units is such as to permit it to be used very effectively with the text, "*New World of Chemistry*," by Bernard Jaffe (reviewed in the JOURNAL OF CHEMICAL EDUCATION, August, 1935, page 399). Nearly all the units are organized according to one definite plan: (1) a *series of experiments* to be performed by the student in the laboratory or by the instructor as demonstrations; (2) a list of several *observations and questions* on the experiments, given in a form intended to compel careful thinking on the part of the student; (3) a shorter list of conclusions given in suggestive form so that the student must deliberate, classify evidence, and summarize results; (4) a large list of *supplementary exercises* intended to provide practice in the application of the principles involved in the experiments and to test understanding of generalizations derived from the unit; (5) a short list of *optional questions* intended to provide worth-while extra work for the abler student. The last five units of the book are intended as exercises in summary and review of some of the most important items of elementary chemistry. Unit 48 consists of several pages devoted to a review of the methods used in solving chemical problems. One page of directions for the preparation of solutions is followed by lists giving exactly the chemicals and apparatus needed for the experiments described in each unit. Additional apparatus needed for demonstration are also given in separate lists.

This book has been very carefully prepared. The authors are clearly fully acquainted with the difficulties of directing high-school laboratory work, and with the best methods of overcoming these difficulties. The experiments are well selected. The *Observations and Questions on Experiments* are true learning exercises, in which the student is forced to look for evidence, to reason and think his way to correct conclusions as far as possible. The supplementary exercises and the optional questions provide much rich material for testing the student's ability to apply the principles learned. These materials may also be used in assigning additional work for the faster or abler student.

The book may be used to advantage in classes using either single or double laboratory periods. Experiments which should be used as demonstrations are indicated in only a few cases. In general, the teacher is permitted to decide just which experiments should be used as demonstrations and which should be performed by the students individually. This will enable each teacher to use the book in the way which best fits his needs, his conditions, and his resources.

One of the most important parts of the book is Unit 48 (which deals with chemical arithmetic, as mentioned above). This unit is not perfect and some of the methods recommended are more or less mechanical, but much excellent work has been done and other authors will find it difficult to equal the unit as a whole.

The reviewer highly recommends this book to all teachers of high-school chemistry.

J. O. FRANK

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A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. *Francis Sutton*. Revised by *A. D. Mitchell*, Scientific Assistant, University of London, and Assistant Editor, *Journal of the Chemical Society*. Twelfth edition. P. Blakiston's Son & Co., Inc., Philadelphia, 1935. xvi + 631 pp. 128 figs. 13.5 × 21.25 cm. $10.00.

It is a pleasure to welcome this (the twelfth) edition of so time-honored a treatise as Sutton's "Volumetric Analysis," seeing that the first issue made its appearance some seventy-odd years ago.

To pronounce the work "comprehensive" would be resorting to a mild expression; for, in addition to the discussion of general principles and the insertion of a number of tables, the authors have treated the following topics: alkalimetry and acidimetry, analysis by oxidation or reduction, analysis by precipitation,

potentiometric titration, applied methods of analysis (inorganic and organic substances), analysis of urine and blood, analysis of water and sewage, and volumetric analysis of gas. But even so, the book may have fallen short of its somewhat pretentious subtitle, wherein it is claimed that the subject matter is "adapted to the requirements of pure chemical research, pathological chemistry, pharmacy, metallurgy, manufacturing chemistry, photography, etc., and for the valuation of substances used in commerce, agriculture, and the arts."

Certainly the present revision shows some marked improvements over the retiring edition, among which may be mentioned the incorporation of theoretical matter in connection with neutralization methods, the addition of a short chapter on potentiometric titration (as already indicated), and the introduction of 8-hydroxyquinoline as a precipitant for either aluminum or magnesium and of potassium periodate as a colorimetric reagent for manganese. It is not difficult to discover minor imperfections here and there: those oxidimetric processes that depend upon the use of a standardized solution of ceric sulfate, because of their great nicety, might well have been allotted more space; iron wire and ferrous ammonium sulfate for establishing the titer of potassium permanganate solutions are hardly to be regarded as reference substances of the first order; the procedure of Wells and Mitchell for the estimation of titanium could have been omitted with propriety on account of the very low results obtained by the original investigators; the reduction methods of Knecht and his disciples, which involve unusual manipulations, are described with too great paucity of detail; but such judgments may be passed upon almost any printed work.

On averaging the more with the less desirable, we are forced to the conclusion that the book under consideration is a remarkably good "storehouse" of information on volumetric analysis. It is safe to say that there are few chemistry libraries without the current volume of "Sutton" on their shelves, where, we hope, it may be found for many a year.

WILLIAM M. THORNTON, JR.

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ORGANIC SOLVENTS, PHYSICAL CONSTANTS AND METHODS OF PURIFICATION. *Arnold Weissberger and Erich Proskauer.* Translated from the German manuscript by *Randal G. A. New.* Oxford University Press, 114 Fifth Ave., New York City, 1935. ii + 210 pp. 15.25 × 23.25 cm. $5.00.

In the preface the authors state: "In recent years improvements in the methods of organic chemistry and the enhanced interest in the chemical physics of non-aqueous solutions have led to an ever-increasing demand for variety and purity in organic solvents." This reason has led the authors to make a collection of physical constants and of methods of purification for these solvents. The aim of this book is to make readily accessible the abundant material which has been accumulated by chemists and physicists in recent years. To this end an organic chemist and a physical chemist have collaborated.

It is the hope of the authors that a study of the systematic list of solvents and of the numerical data, classified systematically, contained in the book will facilitate the choice of the proper solvent to assure the success of physical and chemical work, which is so often primarily dependent on that factor. They have attempted to assemble a list adapted to as many different requirements as possible.

The present is the first edition of the book, which has been translated into English from the original German manuscript.

The contents of the book are divided into four sections: I. Systematic Classification of Solvents; II. Tables of Physical Constants; III. Purification of Solvents; and IV. References to Literature.

The solvents are arranged in order of increasing chemical complexity, according to the following scheme: (A) Hydrocarbons (aliphatic saturated; aromatic; aliphatic unsaturated). (B) Compounds with one type of characteristic atom or group (hydroxy-compounds; esters; amines; etc.). (C) Compounds with more than one type of characteristic atom or group (esters of hydroxy-acids; chloro-alcohols; chloro-amines, etc.). In groups (B) and (C) the substances are arranged according to the nature of the hetero-atom, in the order O, Cl, Br, N, S. One hundred fifty-seven solvents are classified.

Section II lists the more important physical constants of these solvents. Each solvent is taken as the subject of a table which consists of four columns. In the first column each physical constant is denoted by a number which occurs in every table. The second column indicates the special conditions under which the constants have been determined. The third column contains the preferred values for the constant, and the fourth column refers to the list of literature references which comprise Section IV of the book. The constants listed are: 1. Structural formula. 2. Beilstein reference. 3. Molecular weight. 4. Density. 5. Melting or freezing point in °C. 6. Boiling point in °C. 7. Vapor pressure in mm. Hg. 8. Latent heat of evaporation in gram cals./gram. 9. Specific heat in gram cals./gram/°C. 10. Cryoscopic constant in degrees lowering for 1 g. mol. solute in 1000 g. of solvent. 12. Viscosity in c. g. s. units. 13. Electrical conductivity in reciprocal ohms. 14. Dielectric constant. 15. Dipole moment in Debye units (10^{-18} c. s. o.). 16. Refractive index. 17. Ultra-violet absorption. 18. Infra-red absorption. 19. Flash point in °C. 20. Association, hygroscopicity, toxicity, etc. 21. Reference to methods of purification which are the subject matter of Section III.

The authors have accomplished their purpose. The subject matter is well written and splendidly arranged. Tables and printing are clear. Methods of purification are discussed sufficiently for general laboratory practice, and the list of references to the original literature is remarkably complete and up to date. No errors were noted.

It is the opinion of the reviewer that this book would be a valuable addition to the library of any laboratory conducting organic or organo-physical research.

M. H. DASKAIS

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HANDBOOK OF CHEMISTRY AND PHYSICS. *Charles D. Hodgman,* Editor in Chief. Twentieth edition. Chemical Rubber Publishing Co., Cleveland, Ohio, 1935. xiv + 1951 pp. 10.5 × 16.5 cm. $6.00.

The most notable innovations in the twentieth edition of the handbook are those relating to organic compounds. Dr. Austin M. Patterson has prepared a slightly abridged form of the "Definitive report of the commission on the reform of the nomenclature of organic chemistry," *J. Am. Chem. Soc.*, **55**, 3905–25 (1933), under the title, "Rules for the Naming of Organic Compounds," and to it has appended a list of "Prefix Names of Organic Radicals." Dr. Patterson has also revised the nomenclature of the "Physical Constants of Organic Compounds." In so far as possible every organic compound appearing in this table has been named in accordance with the rules laid down by the International Union. Such compounds are indicated by an asterisk. Those not covered by these rules are named as nearly in accordance with them as possible. These features make the handbook the only compact and convenient style book of organic nomenclature now available.

The table of physical constants (organic) has been changed from tabular to dictionary style with considerable saving in space. In the reviewer's opinion convenience of reference is also enhanced. Over 1100 new compounds have been added. A "Formula Index of Organic Compounds" is a further addition.

"The Pronunciation of Chemical Words" (pp. 814–25) has been reprinted by permission from a report of the Nomenclature, Spelling, and Pronunciation Committee of the American Chemical Society, *Ind. Eng. Chem., News Ed.*, **12**, 202 (1934).

Other additions and revisions are "Properties of the Amino Acids"; "X-Ray Spectra" (revised); "Magneto-Optic Rotation"; "Colorimetry" (revised).

OTTO REINMUTH